University of Canterbury
Department of Physics and Astronomy

Selection Rules for Effective Intra-Atomic and Optical Transition Operators in Partly-Filled Shell Ions

A Thesis Submitted for the Degree
of Doctor of Philosophy
in the University of Canterbury

1993

by
Qingsheng Wang

Supervisor : Professor G. E. Stedman

To My Wife

To My Parents

Abstract

The important role played by the operator of time reversal in physics is further extended in this thesis. The time reversal selection rules of Abragam and Bleaney (1970) and Stedman and Butler (1980) have been further extended to higher group levels in a Racah group chain. In the spin-orbit product group $SU_2^S \times SO_3^L$ new selection rules are obtained, which restrict the spin-orbital ranks of many-body operators strictly according to an operator's HT (hermitian conjugation and time reversal) signature. At the symplectic group level, time reversal selection rules restrict the HT-even and HT-odd many-body operators to transform as certain irreps of the symplectic group Sp_{4l+2}. This time reversal symmetry classification combined with the power of group theory methods is very useful for the calculation of many-body interactions. These new results also correct and generalise the previous rules based on hermiticity alone. Such new time reversal selection rules are also applied in perturbation theory. Relativistic corrections arising from Dirac-Foldy-Wouthuysen analysis for electron have been reinvestigated. A new spin-dependent E1 matter-field interaction $H_S' = e\dot{\mathbf{A}} \cdot \mathbf{S} \times \mathbf{p}/2m^2c^2$ has been revealed, and also some new M1 operators. The possible significance of this new operator H_S' has been discussed qualitatively for both intra-configurational and inter-configurational spin-forbidden transitions in the light of time reversal selection rules. The Goldstone diagrammatic perturbation method is used to discuss optical transition processes. The Goldstone diagrams suitable for intra-configurational transitions of the lanthanide ions in crystal and in solutions are discussed. The relationships between Goldstone diagrams, angular momentum diagrams, many-particle coupling, and effective tensor operators are discussed. Other selection rules including the quasi-spin classification of half-filled shells are briefly reviewed, and a quantitative calculation for the crystal field splitting for a half-filled rhenium atom has been carried out with its aid.

Acknowledgement

I am very grateful to Professor G. E. Stedman for the time and effort he put into supervising my Ph.D project. His advice and guidance, together with his helpful criticisms, proved most valuable and are much appreciated.

I would like to thank Professor B. G. Wybourne, my previous supervisor, who led me into this interesting field and continues to give me his advice and help.

I would also like to thank Dr P. H. Butler and Dr M F Reid for their help and many stimulating discussions.

Many thanks to my fellow research students, Hughan Ross, Kumar Vetharaniam, Cindy Lienert, and M. Salam. Especially I have had many interesting and helpful discussions with Hughan Ross.

Finally thanks to my wife and my mother and father, I could not have done anything without their support.

Contents

CHAPTER 1

Introduction

Atomic physics is one of the most fascinating and fruitful branches of physics. At the beginning of this century attempts to understand the simplest atom, the hydrogen atom, and its spectrum helped the birth of modern quantum physics, one of the most important discoveries ever made in the history of physics. Since then progress in atomic physics has always been associated with quantum physics, and it is, in fact, hard to draw a line between quantum physics and atomic physics. Physicists have achieved so much understanding at the atomic level in the microscopic world that atomic physics has matured and attention has focussed progressively on the next two levels of nuclear physics and of sub-atomic particles. After the invention of the laser in the 1960s, the study of the atoms has come into a new age. Armed with this new tool and with the power of computers, we can investigate atoms or ions with much greater precision than ever and gain deeper understanding of atomic systems in various conditions. The interaction between atomic theory and the development of laser physics is illustrated by the increasingly ingenious applications of atomic beams in quantum optics.

In this thesis I will discuss some aspects of atomic physics which are particularly associated on the theoretical side with the applications of symmetry principles in quantum mechanics, and on the experimental side with the intensities of optical transitions in lanthanide systems. The context for the thesis is illustrated on the theoretical side by the review of Judd (1988), and in particular the work of Judd (1962), Ofelt (1962), Wybourne (1968, 1970), Judd and Pooler (1982), Lindgren and Morrison (1982), Stedman and Butler (1980), Moore and Stedman (1990), Reid (1988), and on the experimental side by the analysis of one- and two-photon transition intensities by e.g. Downer and Bivas (1983), Downer *et al.* (1988), Becker *et al.* (1985).

From the practical point of view there are two major concerns in this thesis: the energy level structure of electronic states and the intensities for transitions between these energy levels. Around them are grouped some *theories* which deal with these two problems as discussed in this thesis. They are perturbation theory, group theory including the selection rules given by the space-time symmetries of the physical system, and Dirac theory with its relativistic corrections. The energy level structure of the system (atoms or ions plus uncoupled radiation field) is determined by the eigenvalues and the eigenstates of the system's time-independent Hamiltonian H. Once these energy eigenvalues and eigenfunctions are known, we can treat the matter-field interaction operator (or interaction Hamiltonian) V^t as a perturbation to calculate the transition intensities. For a many-electron system, the time-independent Hamiltonian H is also conveniently treated by perturbation theory. The relativistic corrections not only provide many atomic operators for atomic energy corrections but also give modifications to the matter-field interactions (see chapter 6). All these correction operators are treated as perturbations.

Group theory is a very powerful mathematical tool that has important practical applications in quantum mechanics. When an appropriate group chain is found for a certain physical problem, the states and operators in that problem can all be classified by a set of irreducible representations (irreps), and the interactions can be expanded in terms of a basis set of irreducible tensor operators. The ingredients of the corresponding matrix elements $\langle a|O|b\rangle$ can then be classified using the irreps: $\langle a, \alpha_1\beta_1|O^{\lambda\mu}_{lm}|b, \alpha_2\beta_2\rangle$. The space-time symmetries of the states and operators give important selection rules on matrix elements which govern every aspect of the physical problems. The spatial inversion symmetry leads to the well known Laporte parity rule. One finds that time reversal selection rules (TRSRs) have strong links with the group symmetry of the operators (see chapters 3 and 4). We show that such rules have been comparatively undeveloped and underutilized in our areas of interest. In a certain spin-space group level of description of the electronic states, such as the symplectic group, the TRSRs restrict the symmetry type of the operator and therefore have extra power when combined with the spin-space group theory method for applications. In addition, when parity is broken, the TRSRs still hold.

In the following, I introduce and summarise the contents of this thesis in rather more detail and in the same order as the chapters.

In chapter 2, I discuss and review the perturbative treatment of the energy

level structure and optical transition processes in terms of non-relativistic Goldstone-diagrammatic perturbation theory. Normally the zero-order Hamiltonian of an N-electron system is taken as $H^{(0)} = \sum_{i=1}^{N}(\mathbf{p}_i^2/2m - Ze^2/r_i + u_i)$ which consists of the kinetic energy of the electrons, the potential energy of the electrons within the nucleus' Coulomb field, and within the average electrostatic field of the electrons (which affects each electron equally). This assumes that each electron is otherwise independent of the others, the so-called independent particle model. If this average potential $U = \sum_{i=1}^{N} u_i$ is treated as spherically symmetric, i.e. the central field model, the resulting many-particle eigenfunction of $H^{(0)}$ is an antisymmetrised product (so-called Slater determinant) of the N hydrogen-like spherical harmonic eigenfunctions $\Psi = \phi(1)\phi(2)\cdots\phi(N)$ with $\phi = R_{nl}(r)Y^l_{m_l}(\theta,\varphi)\chi_{m_s}$. The *shell* is labelled by the orbital angular momentum quantum number l and the principal quantum number n. Different shells have different energies (the l–dependence of the energy arising from the non-hydrogenic radial dependence of the potential u_i), but a given shell is highly degenerate with respect to $H^{(0)}$. The electrons can fill an l shell with m electrons, l^m, and the upper bound of m is $4l + 2$. Such a filling denoted by nl^m is called a *configuration.*

The degeneracy of a configuration is lifted by the Coulomb interaction between electrons within the configuration, a two-body and noncentral effect. Thus the first-order correction for $H^{(0)}$ is taken as $H^{(1)}(= V) = \sum_{i<j}^{N} \frac{e^2}{r_{ij}} - U$. In the 1930s, workers in atomic theory mainly considered the electrons' Coulomb interactions within a (dominant) configuration. Later the Coulomb interaction between different configurations was also considered (see e.g. Trees and Jorgensen (1961) and Rajnak and Wybourne (1963)). Lindgren and Morrison (1982) have developed a systematic non-relativistic Goldstone diagrammatic perturbation theory suitable for such problems in atomic physics. In their formalism, the Coulomb interaction can be treated more generally, including Coulomb interaction among all possible configurations (or orbitals), such as valence to valence, core to core, valence to core, valence to virtual, etc. The whole Hilbert space is divided into a model (P) space and the remaining (Q) space, where P includes the dominant configuration(s). The effective Hamiltonian acting within the model space helps to simplify the calculation.

Optical transition processes are also treated by perturbation theory. The inter-configuration transition can be treated in first-order perturbation. Due to the Laporte

parity selection rule the intraconfigurational transitions of the lanthanide ions in crystals and solutions have to be explained by second-order perturbation, i.e. Judd-Ofelt theory (see Judd 1962 and Ofelt 1962), which involves an odd parity static crystal field. Reid and Richardson (1984) have further considered and calculated that the dynamic ligand polarization contributions can be comparable in magnitude to those of the static crystal field terms. The third-order perturbation terms contributing to transition processes in lanthanide ions have been discussed by Wybourne (1968), Judd and Pooler (1982), Downer *et al.* (1988), Burdick *et al.* (1989), Smentek-Mielczarek (1991, 1992) etc. The third-order theory of transition processes has been applied to two-photon absorptions, Raman scattering, and also to further refinement of Judd-Ofelt theory for one-photon absorptions, especially for nominally spin-forbidden transitions (see Downer *et al.* 1988). Reid and Ng (1989) extended the time-independent diagrammatic perturbation formalism of Lindgren and Morrison (1982) to optical transition problems in second-order. Recently Burdick and Reid (1993) have extended the formalism to third-order and quantitative calculations have been carried out giving a new insight into the third-order terms latent in the formalism of Judd and Pooler (1982) and Downer *et al.* (1988), in particular the role of "unlinked diagrams" and of folded diagrams. Discussion about these issues is continuing.

In section 2.1, I review briefly the Goldstone diagrammatic perturbation formalism given by Lindgren and Morrison (1982). In section 2.3 the link between time-independent perturbation and time-dependent perturbation is reviewed and discussed. In section 2.4 this analysis for optical transitions is applied to the lanthanide intraconfigurational transitions, and diagrams suitable for such parity-even transitions up to third-order are selected. They are applicable to one-photon and two-photon absorptions and Raman scattering. Since a novel matter-field interaction H'_S is involved, diagrams associated with H'_S correspond to new spin-dependent optical transition mechanisms. By applying the full linked diagram theorem (Brandow 1967, Lindgren 1974) Burdick and Reid (1993) noted that a disconnected third-order term in Judd and Pooler (1982) and Downer *et al.* (1988) (called by them an effective two-body interaction constructed by three one-body operators) belongs to an "unlinked" diagram. Unlinked diagrams are forbidden in the numerator expansion of diagrammatic perturbation theory in the Abrikosov formulation (Stedman (1990), ch 7). Discussion of this issue is given in section 2.2. In section 2.5 the relationship between the Goldstone diagram and its Jucys-type many-electron angular momentum diagram is analysed.

A practical example is given for the Goldstone diagram suitable for Judd-Ofelt theory, and I use the angular momentum coupling diagram (the SO_3 group) method to re-derive the Judd-Ofelt result. A simplified approach to derive the angular part of any Goldstone diagram in terms of the effective tensor operators is also discussed in section 2.6.

In chapters 3,4,5 I discuss the important TRSRs appropriate for atomic physics, the relationship between the TRSRs and the group symmetry of the operators, and the applications of TRSRs in perturbation theory.

In quantum physics we deal with Hilbert spaces and associated unitary transformations of basis. Time reversal T plays a special role in quantum mechanics. It is distinct from most other symmetry operations in physics. Time reversal T is proved (Wigner 1959) to be a so-called "antiunitary" (unitary and antilinear) operation, $T \equiv UK$ where K is the operation of complex conjugation and U is a unitary operation. When acting on a many-electron state $T^2 = \pm\, \mathbf{1}$ where $\mathbf{1}$ is the identity operator and the sign reflects the number of electrons. This leads (e.g. Wigner 1959) to the result that physical states $|\psi\rangle$ are divided into two classes, *even* system with $T^2|\psi\rangle \equiv \overline{\overline{|\psi\rangle}} = |\psi\rangle$ and *odd* system with $T^2|\psi\rangle \equiv \overline{\overline{|\psi\rangle}} = -|\psi\rangle$; each overbar denotes a time reversal operation. From Dirac's theory of the electron it turns out that (see e.g. Messiah (1962)) for electrons the *even* and *odd* systems correspond to the even and odd number of electrons in the systems respectively. This leads to the so-called *Kramers degeneracy*, i.e. an odd number fermion state $T|\psi\rangle \equiv \overline{|\psi\rangle}$ is orthogonal to $|\psi\rangle$ and these two states are degenerate for a time-even Hamiltonian.

In order to investigate the relationship between time reversal symmetry and group theory we suppose that bra and ket states transform as the same real irrep Λ_1 of the group G_1, and as irreps Λ_2 and Λ_2' of a subgroup G_2 respectively. An operator O transforms as the real irrep Γ (l) of the group G_1 (G_2). The matrix element of the operator O between these two states can be written as $\langle \Lambda_1\Lambda_2|O^{(\Gamma)}|\Lambda_1\Lambda_2'\rangle$. According to Wigner-Eckart theorem of group theory the irrep Γ must be contained in the product $[\Lambda_1 \times \Lambda_1]$ to have a non-zero matrix element. If we define τ_Λ as the time reversal signature of the state under double time reversal, $\overline{\overline{|\Lambda_1\Lambda_2\rangle}} = \tau_\Lambda|\Lambda_1\Lambda_2\rangle$, and τ_o as the time reversal signature of the operator under the joint action of the hermitian conjugation (H) and time reversal (T), $\overline{O^{(\Gamma)\dagger}} = \tau_o O^{(\Gamma)}$, then one can obtain (Abragam and Bleaney 1970) the so-called time reversal selection rule, for a matrix element $\overline{\langle\Lambda_1\Lambda_2|}O^{(\Gamma)}|\Lambda_1\Lambda_2'\rangle$ (which is a linear combination of $\langle\Lambda_1\Lambda_2|O^{(\Gamma)}|\Lambda_1\Lambda_2'\rangle$) not to vanish:

The irrep Γ (of the operator) must be contained in the symmetric (antisymmetric) product $[\Lambda_1 \times \Lambda_1]_{+\,(-)}$ if $\tau_\Lambda \tau_o = +1$ $(-1$ respectively).

Much work has since been done. Stedman and Butler (1980) extended the TRSR to a more general case of all point groups and O_3 group. Stedman (1983) gave a comprehensive discussion of the fundamental implications of space-time symmetries in physics in conjunction with parity violation and CP violation and the selection rules associated with spatial and temporal inversion, especially for photon selection rules. Stedman (1987) also discussed the connections between charge conjugation on the one hand and the time reversal on the other, and also the connection with quasi-spin. Moore and Stedman (1990) have applied the TRSR for general second-order perturbation terms with unequal energy denominators for applications such as spin-lattice relaxation, dephasing time, phonon Raman scattering, Jahn-Teller effect, ligand field induced absorption, etc.

Even so the TRSRs have not been exhausted yet. As shown in this thesis (chapters 3 and 4), see also Wang and Stedman (1992a, 1992b), such arguments can be extended to the product group $SU_2^S \times SO_3^L$. At this product group level, the irreps of the SU_2^S group and of the SO_3^L group correspond to the spin rank κ and orbital rank k respectively for an irreducible double tensor operator $\mathbf{W}^{(\kappa,k)}$ or for multielectronic states. Thus, according to the first TRSR of Wang and Stedman (1992a), the electronic states (say a configuration) will impose the restriction on the spin and orbital ranks of the electronic operator according to the operator's HT signature τ_o.

Coincidentally, from the 1960s till the present, various selection rules based solely on the consideration of hermiticity have been proposed. These hermiticity rules are also intended to restrict the spin and orbital ranks of the tensor operators according to their hermiticity. In chapter 3 I offer (see also Wang and Stedman 1992a,b) counterexamples for each such hermiticity rule. The correct selection rules can only be obtained by the joint action of hermitian conjugation and time reversal, i.e. the spin-orbital ranks of the tensor operators can be restricted within a configuration by their HT signatures. Hermiticity alone cannot give any such restriction.

In chapter 4, I further extend this argument into the higher group level in a group chain suitable at least for atomic physics (or the shell model for nuclear physics). The group chain $U_{4l+2} \supset Sp_{4l+2} \supset SU_2 \times [SO_{2l+1} \supset SO_3]$ was proposed by Racah in 1949 to describe many-electron atomic structure in an LS-coupling scheme. The many-electron states can be classified and labelled by a series of irreps of the groups in this

chain. As mentioned before, the eigenstates of an N-electron zero-order Hamiltonian $H^{(0)}$ with independent and central field models are antisymmetrised Slater determinantal products of N hydrogen-like eigenfunctions, which correspond to a group of shells labelled by nl. If the shell nl contains m electrons we obtain the configuration denoted by nl^m. In group theory we can say that the l^m state transforms as an antisymmetric irrep $\{\overbrace{11\cdots1}^{m}\} \equiv \{1^m\}$ of the unitary group U_{4l+2}. The zero-order Hamiltonian $H^{(0)}$ itself transforms as the identity irrep $\{0\}$. The angular momentum coupling with LS-coupling scheme within l^m electrons can be classified according to Racah's group chain, and some of the irreps in that chain correspond to good quantum numbers such as the eigenvalues of the total spin angular momentum $\mathbf{S}^2$ and orbital angular momentum $\mathbf{L}^2$. Accordingly, the operators acting within these states can also be classified and labelled. In other words, the operator must also transform under a certain symmetry type specified by the irreps in that group chain to have non-zero matrix elements. Once the symmetry types of both the states and the operator are known, the calculation of a physical problem related with a matrix element can be carried out in terms of group theory. Thus the symmetry classification for many-body operators is important.

Much work has gone into classifying many-body operators in a group chain. For example, one of the most important interactions in atomic (or nuclear) physics is the Coulomb interaction among the electrons, especially among the valence electrons. Its symmetry properties were investigated by Racah (1949) in the group chain $SO_7 \supset G_2 \supset SO_3$ for f-shell electrons. Later the two-body Trees operators were also classified in a similar way by Rajnak and Wybourne (1963). Difficulties in identifying the operator's symmetries at a higher group level, say the Sp_{4l+2} group symmetries, arise because those lower level symmetries may correspond to (or come from) different irreps at the Sp_{4l+2} group level. Thus any possible classification according to some reasonable physical consideration in the group level $U_{4l+2} \supset Sp_{4l+2}$ would be very helpful. Judd *et al.* (1982) proposed an orthogonality consideration which leads to the conclusion (see e.g. in section 4.1) that an *orthogonal* n-body operator (acting within fermion states) will transform distinctively as an irrep $\{1^n;1^n\}$ of the U_{4l+2} group. Later Judd and Leavitt (1986) and Leavitt (1987) further classified the symplectic symmetries of the many-body operators according to their *hermiticity* selection rules. Unfortunately, as mentioned already (see chapter 3 and Wang and Stedman 1992a,b),

hermiticity alone cannot impose any such selection rule in the $SU_2^S \times SO_3^L$ group, or at the Sp_{4l+2} group level. However, such classification can be achieved by the TRSR under a joint action of hermitian conjugation and time reversal instead. In section 4.3 of chapter 4, I extend such TRSRs into the symplectic group level, and correct and generalise Judd and Leavitt's classification in the Sp_{4l+2} level, i.e. the many-body operators in the symplectic group level can be divided into two classes: *HT-even* and *HT-odd* many-body interactions. Both of them are of physical importance. Many of these HT-even many-body operators have distinct symmetries from HT-odd ones (see Table 4.2). Some possible usage of such time reversal classifications of many-body operators have been discussed in section 4.5 for applications such as Newman's (1971) rule for the ranks of operators contributing to the correlation crystal field within the superposition model, and in section 4.6 for atomic spectra induced by the Coulomb interaction and Trees operators.

In chapter 5 I discuss the application of the TRSRs in perturbation theory, in particular for second-order perturbation. This work is basically an extension of Moore and Stedman (1990) and chapters 3 and 4 (also Wang and Stedman 1992a,b). Many physical applications are discussed as perturbations such as Judd-Ofelt theory and Trees correction terms. To apply the TRSR in perturbation theory is not a trivial problem. Since the essential condition for a TRSR is that the ket and bra states (initial and final states) must transform as irreps of a group which are complex conjugate, or the same real irreps, we will define an effective operator O_{eff} acting between initial and final states. If and only if O_{eff} has a definite HT signature ($+1$ or -1) under the joint action of hermitian conjugation and time reversal, a definite TRSR can be obtained. A general discussion for one-body case is given in section 5.1, and the result can be applied to Judd-Ofelt theory. The even-rank rule obtained by Judd and Ofelt (1962) is reviewed in detail in section 5.2, and a comparison with the conclusion of the TRSR is made. In section 5.4 the gauge transformation of the Judd-Ofelt theory is discussed in the light of the TRSR. Such analysis has not been fully discussed before. In section 5.5, the TRSR appropriate for second-order Coulomb interaction and associated application and complication for Trees operators are discussed.

The relativistic corrections to atomic physics according to Dirac theory, especially the possible spin-dependent radiation-matter interactions and their behaviour under gauge transformation, are discussed in chapter 6. Usually the radiation-matter interaction is obtained from a non-relativistic Hamiltonian minimally coupled with

an electromagnetic field. In the E1 limit, radiation-matter interaction is in the well known form $H_A = -e\mathbf{A}\cdot\mathbf{p}/m + (e^2/2m)\mathbf{A}^2$ in the velocity gauge and $H_E = -e\mathbf{E}\cdot\mathbf{r}$ in the length gauge. There is an ongoing controversy about the compatibility of these two interaction operators in the two gauges. Typically Lamb *et al.* (1987) summarised this problem in their paper with: "*It is perhaps surprising to note that one of the outstanding problems of modern quantum optics is the choice between the two matter-field interaction Hamiltonians which are commonly used:* $-e\boldsymbol{E}\cdot\boldsymbol{r}$ *and* $-e\boldsymbol{A}\cdot\boldsymbol{p}/m + (e^2/2m)\boldsymbol{A}^2$. $\cdots$ *For example, Jaynes nicely summarized the problem in 1976 saying: '*$\cdots$ *a whole generation of physicists has stumbled on this problem and lived, not only under the shadow of immediate difficulty: 'How can I ever know whether a practical calculation has been done right?,' but deeper mystery: 'How it is possible that a theory, for which formal gauge invariance is proved easily once and for all, can lead to grossly noninvariant results as soon as we try to apply it to the simplest real problem?*" Apart from this problem, even after the examination of the relativistic corrections in a Dirac-Foldy-Wouthuysen analysis (see e.g. Drake (1971) and Sebastian (1981)) the conclusion was that in the length gauge, the matter-field interaction is spin-independent and H_E is sufficient. In chapter 6, the Dirac-Foldy-Wouthuysen analysis and the corresponding gauge transformations from the velocity gauge to the length gauge are re-examined for the simplest case, a one electron system. It was found (see chapter 6 and Wang and Stedman 1993) that there exists an extra E1 matter-field interaction $H'_S = e\dot{\mathbf{A}}\cdot\mathbf{s}\times\mathbf{p}/2m^2c^2$ which is spin-dependent. Other new matter-field interaction terms at higher multipole orders also exist, and some of these including their gauge dependence are discussed in connection with the above mentioned controversies. Our new spin-dependent light-matter interaction Hamiltonian H'_S could have implications for the nominal spin-forbidden transition in heavier elements and the real spin-forbidden transition in helium.

Chapter 7 represents the first part of the work of this thesis, and was done under the supervision of Professor B. G. Wybourne. In section 7.1, the special properties of half-filled shells and the explanation in terms of quasi-spin are briefly reviewed following Wybourne (1991), and used in the particular problem of the ground state splitting in the rhenium atom (with a half-filled shell). Pellow *et al.* (1989) reported having deduced the ground state splitting ($\sim 7 \pm 3cm^{-1}$) of the rhenium atoms in krypton matrix from magnetic circular dichroism (MCD) measurements, and suggested that the splitting is due to the mixing of the ground state $^6S_{5/2}$ with $^4P_{5/2}$. Such con-

sideration is oversimplified, and cannot lead to any such crystal field splitting (see Wang and Wybourne (1990) and chapter 7). If the splitting is real, the higher order perturbation which involves many more states, even with other configurations, must be considered. In section 7.2 a quantitative calculation for the crystal field ground state splitting for a half-filled rhenium atom has been carried out.

CHAPTER 2

Diagrammatic Perturbation Analysis of the Optical Transition Processes Up To the Third-order

In this chapter we will discuss perturbation theory for optical transition processes for lanthanide ions in crystals and solutions, including one-photon absorption, two-photon absorption, and electronic Raman scattering. Sharp spectral lines are seen in absorptions and Raman scattering. These were attributed to the atomic $4f^N \rightarrow 4f^N$ transitions ($\Delta L, \Delta J \leq 6$), since $4f$ states are protected from the broadening influences of the crystalline environment by the $5s^2 5p^6$ shield; the partially filled (open) $4f$ shell of the lanthanide ions in crystals has a less extended radial wavefunction than filled $5s^2 5p^6$ shell. However, such intra-configuration transitions require an *even parity* transition operator. The odd-parity electric dipole $-e\mathbf{E} \cdot \mathbf{r}$ alone cannot contribute while magnetic dipole and electric quadrupole are too weak. To solve this puzzle another odd-parity interaction must be invoked to form with the electric dipole operator an even-parity effective operator. To do so second-order perturbation theory must be invoked and the odd-parity crystal field V_O proves to be the appropriate partner in many crystal and liquid environments. Judd (1962) and Ofelt (1962) formulated such second-order theory in terms of effective tensor operators. The parameterized quantitative fittings of a large number of experimental data throughout the lanthanide series have been carried out according to this theory and have given overwhelming support to this theory.

The experimental observations of the two-photon transitions in the lanthanide ions show analogues in many ways to the one-photon process (e.g. see Downer and Bivas 1983). Strong and sharp intra-configuration transitions within the $4f$ shell with $\Delta L, \Delta J \leq 6$ are observed. Two electric dipole interactions in second-order perturbation form a parity-allowed transition operator; however, its tensor rank can only

permit transitions with $\Delta L, \Delta J \leq 2$. Again one has to move to higher order perturbation (third-order) to seek satisfactory transition operators for operator ranks of $\Delta L, \Delta J \leq 6$ (Judd and Pooler (1982), Downer *et al.* (1988), Burdick *et al.* (1989)). The basic strategy is to incorporate spin-orbit interaction (even-parity) at third-order perturbation with the two electric dipole interactions. It was also realised initially by Wybourne (1968) that such third-order terms also play a role in the one-photon transitions. This third-order effect is particularly important for the one-photon spin-forbidden transitions, $\Delta S = 1$, and the refinements of second-order Judd-Ofelt theory have been discussed by Downer *et al.* (1988). In these applications a second quantisation method for deriving the effective tensor operators (see Judd 1967) has been used.

In third-order perturbation, two-body interactions such as the Coulomb interaction can also be involved. The method used by Judd and Pooler (1982) and Downer *et al.* (1988) has difficulties in treating such problem systematically. The perturbation theory can be treated in a systematic way by means of non-relativistic field theory. The Feynman-diagram-like method called the Goldstone diagram technique was originally developed in a time-dependent perturbation theory by Goldstone (1957). Lindgren (1974) applied such techniques to a time-independent problem, that of energy level structure in atomic physics. A similar application was also made to nuclear systems by Brandow (1967). Diagrammatic perturbation theory is based on two important theorems, Wick's theorem and the linked diagram theorem. The linked diagram theorem has been proved for both time-independent perturbation (Brandow (1966, 1967), Sandars (1969), Lindgren (1974, 1978)) and time-dependent perturbation (Goldstone (1957), Morita (1963), Oberlechner *et al.* (1970), Kuo *et al* (1971), Johnson and Baranger (1971), Stedman (1990)) and for various cases (non-degenerate closed-shell or degenerate open-shell systems). The operators derived by Judd and Pooler (1982) and Downer *et al.* (1988) can be identified in terms of appropriate Goldstone diagrams. A possible confrontation with the full linked diagram theorem will be discussed in section 2.2. This problem is still open for further study. Recently Burdick and Reid (1993) have reached the conclusion: that one of the effective two-body operators (see Fig. 2.4) derived by Judd and Pooler (1982) and Downer *et al.* (1988) violates the full linked diagram theorem. They have also carried out essentially a related approach to the many-body analysis as ours in this chapter and have independently carried it through to extensive quantitative calculations and com-

parisons with experiment. Their results show that good agreement with experiment is achieved by using the electron correlation diagrams (two-body diagrams) when the "unlinked" effective two-body operators (Fig. 2.4) used previously are excluded.

Perturbation theory (see e.g. Lindgren and Morrison 1982) applies to a physical system whose Hamiltonian H can be written as two parts: $H = H_0 + V$ where H_0 is a zero-order or model Hamiltonian which is an approximation to the full Hamiltonian, and V is regarded as a *perturbation.* The eigenfunctions of the model Hamiltonian form a complete Hilbert space. One (or a group of) eigenfunction(s) of the model (zero-order) Hamiltonian can be chosen as the *model space* (P space), and the remainder of the eigenstates form the *orthogonal space* (Q space). Then the *effective Hamiltonian* H_{eff} acting only within the model space can be defined, and its eigenvalue is the exact energy. The choice of the model space depends on the physical problem. Such formalism can be expanded in a perturbation expansion, i.e. the eigenvalue of the nth-order effective Hamiltonian is the nth-order exact energy of the system. There are two popular perturbation expansions. The Brillouin-Wigner perturbation expansion explicitly includes at each order the initially unknown exact energy, while the Rayleigh-Schrödinger expansion uses the unperturbed energies. The latter is preferable for many physical applications and is amenable to the Goldstone diagram method. For time-independent applications in atomic physics, such a Goldstone-diagrammatic perturbation theory has been given by Lindgren and Morrison (1982) (see section 2.1). In section 2.3 the linkage between the time-independent and time-dependent perturbations is reviewed and discussed. We extend the use of formalism of Lindgren and Morrison (1982) to optical transition processes. In order to reduce the number of diagrams that we have to deal with we make an approximation that only the valence electron excitations are considered and all core excitations are ignored.

In atomic physics, the zero-order Hamiltonian H_0 of the system is chosen (let $\hbar = e = m = 1$) as $H_0 = \sum_{i=1}^{N}[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}] + U$ where $U = \sum_i u(r_i)$ is the average (general unrestricted Hartree-Fock) potential that each electron feels, and it is treated as spherically symmetric (central-field approximation). The eigenfunctions of H_0 are members of *configurations* denoted by nl^m, i.e. the principal quantum number n, the orbital angular momentum quantum number l, and m the number of electrons in the shell. The model space of this atomic system can be chosen as one configuration or

as several strongly interacting configurations.

In addition, under the central-field approximation, unperturbed (zeroth-order) states are separated into the radial part and the orbital part. Therefore the matrix element of an effective Hamiltonian in any order of perturbation within the model space can be evaluated in three parts, the radial part which may be represented by parameters, the reduced orbital part, and an angular part. Furthermore the angular part of a particular perturbation interaction can be represented by an angular momentum coupling diagram which may be topologically identical to the corresponding Goldstone diagram provided that many-particle coupling is ignored and all interactions involved are spin-independent.

However, in practice even if all interactions are spin-independent, the many-particle state coupling (N electrons within the same shell nl, i.e. the configuration nl^N) still arises from the Coulomb correlation, and thus the angular diagram will not be topologically identical to the corresponding Goldstone diagram. In that case one should decompose any intermediate many-particle state into one-particle components, only one of which interacts at one time. The condensation of the angular momentum coupling into a single vertex as for the Goldstone diagram strictly requires a closure approximation for the intermediate states. In this case the angular part can be further simplified as a set of nj symbols multiplied by an *effective tensor operator* acting only between the initial and final fully coupled (many-particle coupling) states. Then part of the total angular-diagram, i.e. disregarding the many-particle coupling for the initial and final states, is topologically identical to the corresponding Goldstone diagram provided that there is no spin-dependent interaction involved. We will give a detailed account in section 2.4. This effective (tensor) operator should not be confused with the effective Hamiltonian. Such an effective tensor operator formalism can be found in, for example, Judd-Ofelt theory (Judd 1962, Ofelt 1962), the second-order Coulomb interaction (see Wybourne 1968) for second-order perturbation, and Downer *et al.*'s (1988) third-order perturbation theory. There are three equivalent methods to derive the angular part of an effective interaction in terms of effective tensor operators: (1) the tensor product method (see Wybourne 1968), (2) the second quantisation method (Judd (1967), Judd and Pooler (1982), Downer *et al.* (1988)), (3) and in section 2.4 of this chapter we can use a technique which we term the angular diagram technique, and which has computational efficiency for third-order terms. This technique is directly related to the corresponding Goldstone diagram.

Apart from the problems mentioned above, two other important issues will not be discussed in this chapter. One is the time reversal selection rule (TRSR) that every operator has to obey. A discussion of this will form the contents of chapters 3, 4, and 5. Its importance goes beyond the optical transition itself, and the associated selection rules are universal in physics. Another is the matter-field interaction operator itself. It is well known (but not well understood) that the electric dipole operator $H_E \equiv -e\mathbf{E}\cdot\mathbf{r}$ is an equivalent length gauge counterpart of $H_A \equiv -\frac{e}{m}\mathbf{A}\cdot\mathbf{p} + \frac{e^2}{m}\mathbf{A}^2$ in the velocity gauge. For practical reasons, many people prefer to work within the length gauge, and for a long time only one matter-field interaction H_E has been used to calculate the spin-allowed and spin-forbidden optical transition intensities. The controversy about the compatibility of H_A and H_E in two gauges still continues. This issue will be discussed in chapter 6, and we will show that H_A and H_E may be compatible when a non-relativistic limit and the E1 limit are taken for the system Hamiltonian, and the radiation field is treated as a classical field. However, if the relativistic corrections are taken into account, there are some complications which are not well known or even not noted previously. First, the spin-orbit interaction $V_{SO} \equiv \lambda\mathbf{S}\cdot\mathbf{L}$ and a less well known matter-field interaction $H_T \equiv -e\lambda\mathbf{A}\cdot\mathbf{S}\times\mathbf{r}$ appear in the velocity gauge simultaneously (Drake 1971,1972). For a single particle system $\lambda = e^2/8\pi\epsilon_0 m^2c^2r^3$. Under a gauge transformation H_T is cancelled out exactly in the length gauge in first-order. However, we will show that in higher order perturbation (higher than first-order) an operator of the same algebraic form as H_T will also play an important role in the length gauge for spin-forbidden transitions. Second, another spin-dependent matter-field interaction $H'_S \equiv \chi\boldsymbol{\sigma}\cdot\mathbf{E}\times\mathbf{p}$ also appears in the same term as the spin-orbit interaction in the E1 limit. The importance of these novel spin-dependent matter-field interactions and their applications in atomic physics will be discussed in chapters 6.

Our aim in this chapter is, first, to give a brief review of the Goldstone diagram perturbation theory (Lindgren and Morrison 1982) including Wick's theorem, the closed diagram theorem, and the full linked diagram theorem in section 2.1. Second, a problem related to the linked diagram theorem and disconnected effective Hamiltonian diagrams will be discussed in section 2.2. Third, a systematic Goldstone diagram perturbation analysis up to the third-order suitable for the formulation of intra-configuration transition intensities is discussed in section 2.3 and 2.4. Fourth, in many-particle system the linkage between the Goldstone diagram for effective Hamiltonian and the angular momentum coupling diagram of such interactions will be

discussed for example for Judd-Ofelt theory in section 2.5. A simplified diagrammatic method of deriving the effective tensor operators will be given in section 2.6. Using this simplified diagrammatic method the formulation of all Goldstone diagrams for intra-configuration transition intensities for the lanthanide ions can be derived in terms of the effective tensor operators. They are discussed in section 2.6.

2.1 Goldstone diagrammatic perturbation theory

We now discuss some basic ingredients of Rayleigh-Schrödinger perturbation theory and the corresponding diagram method. Details can be found in Lindgren and Morrison (1982). We write the eigenfunctions of the model (zero-order) Hamiltonian as $|\phi^i\rangle$:

$$H_0|\phi^i\rangle = E_0^i|\phi^i\rangle, \qquad \langle\phi^i|\phi^j\rangle = \delta(i,j).$$

All of these eigenstates form a Hilbert space of H_0. In the degenerate case there may be several independent eigenstates $|\phi^\alpha\rangle$ corresponding to the same eigenvalue, say the ground eigenstate E_0^g, and these eigenstates can be chosen as the model space P which is a subspace of the whole Hilbert space. The eigenfunctions in the model space are not automatically orthogonal, but they can be orthogonalized by the Schmidt procedure. Thus the remaining part of the whole Hilbert space is called the orthogonal space or the Q space. The projection operators for P and Q spaces are defined as

$$P = \sum_{\alpha\in P} |\phi^\alpha\rangle\langle\phi^\alpha|, \qquad Q = \sum_{\beta\notin P} |\phi^\beta\rangle\langle\phi^\beta|, \tag{2.1}$$

and $P+Q=1$. In the central-field approximation of atomic physics, the model space represents one or several strongly interacting configurations.

If the model space has d dimensions, it can be shown that there is a one-to-one correspondence between d eigenfunctions of the full Hamiltonian Ψ^a and their projections onto the model space,

$$\Psi_0^a = P\Psi^a, \qquad (a = 1, 2, \cdots, d).$$

It is also possible to define an operator Ω (called *the wave operator*) performing the reverse,

$$\Psi^a = \Omega\Psi_0^a, \qquad (a = 1, 2, \cdots, d),$$

which transforms all the model states back to the exact states. It has been proved (Lindgren 1974, 1978; Kvasnicka 1974, 1977) that in general the wave operator satisfies

the following equation,

$$[\Omega, H_0]P = V\Omega P - \Omega PV\Omega P \tag{2.2}$$

which is referred to as the *generalised Bloch equation.* This equation is exact and *completely equivalent to* the (time-independent) Schrödinger equation $H\Psi^a = E^a\Psi^a$. The wave operator Ω can be expanded (in Rayleigh-Schrödinger theory) as

$$\Omega = \Omega^{(0)} + \Omega^{(1)} + \Omega^{(2)} + \cdots, \tag{2.3}$$

where $\Omega^{(0)} = 1$, and we obtain, order by order,

$$\begin{aligned}
[\Omega^{(1)}, H_0]P &= QVP, &(2.4)\\
[\Omega^{(2)}, H_0]P &= QV\Omega^{(1)}P - \Omega^{(1)}PVP, &(2.5)\\
[\Omega^{(3)}, H_0]P &= QV\Omega^{(2)}P - \Omega^{(2)}PVP - \Omega^{(1)}PV\Omega^{(1)}P, &(2.6)\\
&\cdots\cdots.
\end{aligned}$$

Now we can introduce the *effective Hamiltonian* as the following. The exact solution of the eigenfunctions and the eigenvalue of the Schrödinger equation $H\Psi^a = E^a\Psi^a$ are unknown. Supposing that Ψ^a $(a = 1, 2, \cdots, d)$ are part of the exact eigenfunctions of the full Hamiltonian and their projection on the model space are Ψ_0^a, the Schrödinger equation can be written as

$$H\Omega\Psi_0^a = E^a\Psi^a.$$

By applying the projection operator P from left on this equation one obtains

$$PH\Omega\Psi_0^a = E^a\Psi_0^a.$$

Thus the original exact Schrödinger equation can be rewritten as

$$H_{eff}\Psi^a = E^a\Psi_0^a, \qquad H_{eff} = PH\Omega P. \tag{2.7}$$

Then the *effective Hamiltonian* H_{eff} of the system can be introduced, which operates entirely within the model space. This implies that *the eigenvectors of the effective Hamiltonian represent the model functions and the eigenvalues are the exact energies of the corresponding true states.* Since the wave operator has been expanded in terms of the perturbation V in eqns. (2.3) $\cdots$ (2.6), from order to order of perturbation

expansion we have

$$H_{eff}^{(0)} = PH_0P, \tag{2.8}$$

$$H_{eff}^{(1)} = PVP, \tag{2.9}$$

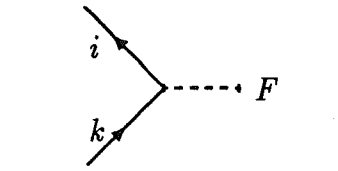
$$H_{eff}^{(2)} = PV\Omega^{(1)}P, \tag{2.10}$$

$$H_{eff}^{(3)} = PV\Omega^{(2)}P, \tag{2.11}$$

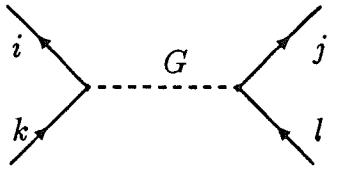
$$\cdots\cdots.$$

We can see that the wave operator $\Omega^{(n)}$ can be solved from lower order to higher order step by step, and the nth-order effective Hamiltonian $H_{eff}^{(n)}$ is basically the product of the perturbation operator V and the $(n\text{-}1)$th-order wave operator $\Omega^{(n-1)}$.

In the second quantisation formalism any n-body interaction can be written graphically. For the one-body (F) and the two-body (G) interactions for example we have



$$\Rightarrow \qquad F = \sum_{i}^{N} f_i = \sum_{ik} a_i^\dagger a_k \langle i|f|k\rangle,$$



$$\Rightarrow \qquad G = \sum_{i<j}^{N} g_{ij} = \tfrac{1}{2}\sum_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \langle ij|g|kl\rangle.$$

Here an annihilation operator a_l destroys a particle from the orbital l ($lm_l sm_s$), connecting this state to the vacuum, and a creation operator $a_j^\dagger$ creates a particle from the vacuum in orbital j ($l'm_l's'm_s'$). In the atomic shell model the electrons fill the eigenstates (configurations) of zero-order Hamiltonian according to the Pauli principle. These eigenstates (configurations) can be classified as

a) core orbitals, *fully occupied by electrons*;

b) valence orbitals, *partially occupied*;

c) virtual orbitals, *unoccupied.*

The valence and the virtual states are defined as the "particle states". Partially filled valence states are called *open shell* states, as opposed to *closed shell.* In a particle-hole formalism, annihilating a core state is equivalent to creating a *hole* in fully occupied core states.

Following Goldstone (1957), in a Goldstone diagram the core orbitals and the virtual and valence particle states are distinguished by the lines directed by an arrow

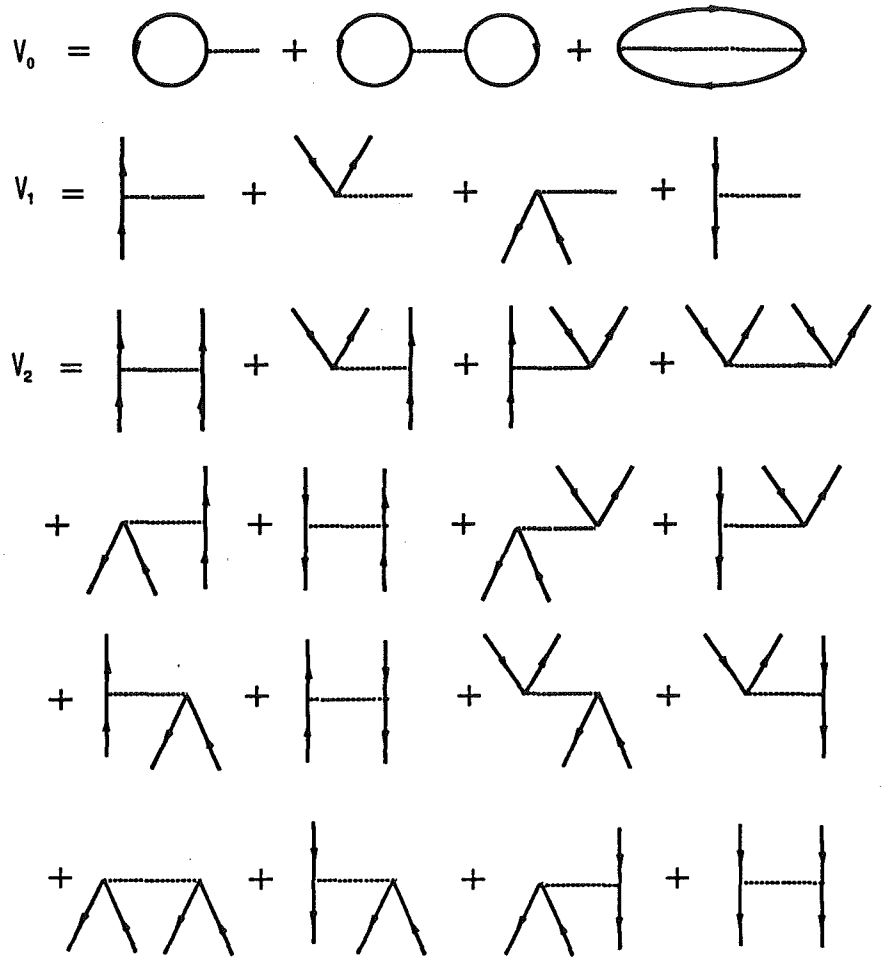


Figure 2.1 Goldstone diagrams of the perturbation operator V

downwards and *upwards* respectively. A downward core orbital line also represents a hole moving in the opposite direction, and is said to denote both core and hole states. In terms of time history, according to the Goldstone rule, the "particle states" are represented by an upward line in the *direction of increasing time*, but the core states in the *direction of decreasing time*. Hence for all of the Goldstone diagrams "the direction of increasing time is upwards" (Goldstone 1957), and the above two diagrams may be interpreted as the interactions within the particle states only. Other possible interactions among the "particles" and core electrons form a variety of Goldstone diagrams (see for example Fig. 2.1). In the following if necessary Roman letters $(ijk\cdots)$ are used to denote the particle states, and Greek letters $(\alpha\beta\gamma\cdots)$ for the core (hole) states. The interactions of the core electrons with the "particles" (or even with themselves) via the Coulomb interaction is called the *core polarisation*.

For the closed shell case, there are no valence orbitals. For the open shell case, it is necessary to indicate the valence states only by an upwards line directed by *double arrows*. In this way, all of the operators, such as V and $\Omega^{(n)}$, (e.g. eqns. (2.5) (2.7) (2.11) etc) can be presented in terms of the Goldstone diagrams. The perturbation expansion of the effective Hamiltonian $H_{eff}^{(n)}$, order by order, becomes the graphical product of V and $\Omega^{(n-1)}$.

Lindgren and Morrison (1982) are concerned with the energy structure of atomic system, such as the hyperfine structure etc. In that case, by using the diagrammatic perturbation theory, the core polarization effect can be fully investigated. The Coulomb interaction among core electrons and valence electrons is strong enough to influence the energy level structure. We will follow through some discussions of Lindgren and Morrison (1982) since their formalism will be used in section 2.3 for optical transition intensities.

In the case of the energy level structure of an atomic system in a time-independent perturbation theory, the model Hamiltonian is taken as $H_0 = \sum_{i=1}^{N}[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + u(r_i)]$. The perturbation V is taken as the Coulomb interaction V_{es} minus U, $V = \sum_{i<j}^{N}\frac{e^2}{r_{ij}} - U$ since the strong Coulomb repulsion among the electrons will influence the energy structure most and the zero-order Hamiltonian has not taken this effect into account fully. This perturbation V can be separated as the effective zero-body V_0, one-body V_1, and two-body V_2 terms as

$$V = V_0 + V_1 + V_2. \tag{2.12}$$

In the second quantisation formalism they can be written as

$$\begin{aligned}
V_0 &= \sum_{\alpha}^{core}\langle\alpha| - u|\alpha\rangle + \frac{1}{2}\sum_{\alpha\beta}^{core}[\langle\alpha\beta|\frac{e^2}{r_{12}}|\alpha\beta\rangle - \langle\beta\alpha|\frac{e^2}{r_{12}}|\alpha\beta\rangle], \\
V_1 &= \sum_{ij}\{a_i^\dagger a_j\}\langle i| - u|j\rangle + \sum_{ij}\{a_i^\dagger a_j\}\sum_{\alpha}^{core}[\langle i\alpha|\frac{e^2}{r_{12}}|j\alpha\rangle - \langle\alpha i|\frac{e^2}{r_{12}}|j\alpha\rangle], \\
V_2 &= \frac{1}{2}\sum_{ijkl}\{a_i^\dagger a_j^\dagger a_l a_k\}\langle ij|\frac{e^2}{r_{12}}|kl\rangle.
\end{aligned} \tag{2.13}$$

These in turn can be presented in terms of the Goldstone diagrams shown in Fig. 2.1. It is noted that V_1 vanishes if the Hartree-Fock potential is used. The Coulomb interaction as a perturbation will split the configuration into different energy terms. From the group theory point of view, the model Hamiltonian $H_{eff}^{(0)} = PH_0P$ transforms as

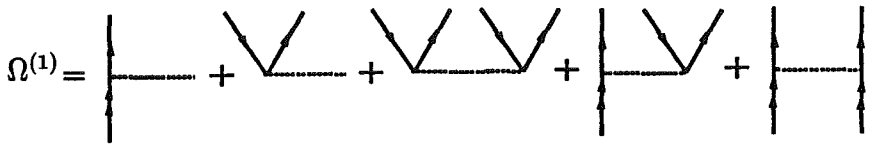


Figure 2.2 Goldstone diagrams of the first-order wave operator $\Omega^{(1)}$

the irreducible representation (irrep) of the unitary identity $\{0\}$, the first-order effective Hamiltonian $H_{eff}^{(1)} = PVP = PV_0P + PV_2P$ is the Coulomb interaction, PV_0P also transforms as the irrep $\{0\}$ of U_{4l+2} (unitary identity), and PV_2P transforms as the irrep $\{11;11\}$ of U_{4l+2} and is a scalar (irrep (0)) in SO_3. The PV_0P part affects only the centre of gravity of the spectrum. A parallel discussion of the symmetry properties of the Coulomb interaction and other interactions will be given in chapter 4.

The wave operator Ω can also be presented in terms of Goldstone diagrams. Ω can be written as

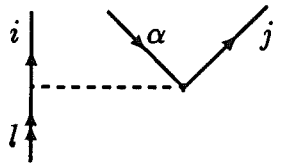
$$\Omega = 1 + \Omega_1 + \Omega_2 + \Omega_3 + \cdots, \tag{2.14}$$

where Ω_i is an i-body operator which should not be confused with the nth-order perturbation expansion $\Omega^{(n)}$ (eq.(2.3)),

$$\begin{aligned} \Omega_1 &= \sum_{ij} \{a_i^\dagger a_j\} \chi_j^i, \\ \Omega_2 &= \sum_{ijkl} \{a_i^\dagger a_j^\dagger a_l a_k\} \chi_{kl}^{ij}, \\ \Omega_3 &= \sum_{ijklmn} \{a_i^\dagger a_j^\dagger a_k^\dagger a_n a_m a_l\} \chi_{lmn}^{ijk}, \end{aligned} \tag{2.15}$$

where the curly brackets denote that the operators within are in normal order (or normal form), i.e. $a_{core}^\dagger$ and a_{virt} appear to the right of a_{core} and $a_{virt}^\dagger$. Lindgren and Morrison (1982, p291) shown that for the open shell case the wave operator Ω can only annihilate the core and valence states, and can only create the virtual states. According to the Bloch equation (eq. 2.2) each Ω_i will be associated with an energy denominator $D = \sum(\epsilon_{in} - \epsilon_{out})$ where $\sum \epsilon_{in}$ ($\sum \epsilon_{out}$) represents the energies of the incoming (outgoing) orbital lines. In a perturbation expansion the first-order wave operator $\Omega^{(1)}$, for example, has to satisfy eq. (2.4), $[\Omega^{(1)}, H_0]P = QVP$. Therefore $\Omega^{(1)}$ is restricted by the diagram representations of the perturbation operator V, which satisfy the conditions that such diagrams can only annihilate the core and valence

states and only create the virtual states. Thus the diagram representations of the first-order wave operator can be chosen from Fig. 2.1 and are shown in Fig. 2.2. We can evaluate each of them. For example



$$= a_i^\dagger a_j^\dagger a_\alpha a_l \frac{\langle ij|\frac{e^2}{r_{12}}|l\alpha\rangle}{\epsilon_l+\epsilon_\alpha-\epsilon_i-\epsilon_j}.$$

The graphical representations of the perturbation term V and the first order wave operator $\Omega^{(1)}$ are the basic building blocks to form second-order effective Hamiltonian $H_{eff}^{(2)}$ (eq. 2.10) and second-order wave operator $\Omega^{(2)}$ (eq. 2.5). Such a procedure is carried out order by order.

Before performing the diagrammatic perturbation expansion, we must discuss some important theorems in diagrammatic perturbation theory. They are crucial for carrying out any diagrammatic expression of an equation such as eq. (2.11).

(i) **Wick's theorem for operators products** If A and B are two operators consisting of creation and annihilation operators in normal order, the product of A and B can be expressed as

$$AB = \{AB\} + \{\widehat{AB}\}, \tag{2.16}$$

where the first term has no contraction between A and B, and the second term has all possible contractions between A and B. In terms of the graphical representation the product AB is the sum of diagrams obtained by joining lines at the bottom of the diagram of A with lines at the top of the diagram of B in all possible ways so that the direction of the arrows is continuous.

(ii) **Closed diagram for open shell** A *closed diagram* for the open shell is defined as *a diagram that has no other free lines than valence lines.* Otherwise the diagram is said to be *open.* The closed diagrams will operate within the P space and the open diagrams will connect the P and Q spaces. Thus it is concluded that *for any operator O the diagrams for POP are closed and the diagrams for QOP and POQ are open. The effective Hamiltonian H_{eff} is represented by closed diagrams.*

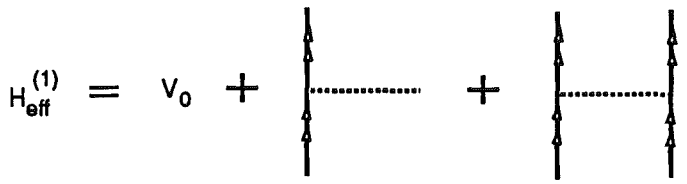


Figure 2.3 Goldstone diagrams of the first-order effective Hamiltonian $H_{eff}^{(1)}$

These two theorems allow the effective Hamiltonians to be constructed. Since $H_{eff}^{(1)} = PVP$, only the closed diagrams in Fig. 2.1 correspond to PVP, and they are shown in Fig. 2.3.

The second-order effective Hamiltonian $H_{eff}^{(2)}$ satisfies $H_{eff}^{(2)} = PV\Omega^{(1)}P$ where $V\Omega^{(1)}$ is a graphical product of V (Fig. 2.1) and $\Omega^{(1)}$ (Fig. 2.2) according to Wick's theorem. Such products are closed by two projection operators P (no other free lines than the valence lines). If the graphical product of two operators A and B is separated (one of the possible result of Wick's theorem), such a diagram is called *disconnected.* We can see that V and $\Omega^{(1)}$ are all *connected.* According to Lindgren and Morrison (1982, p298), in closing a diagram, all free lines which are not valence lines must be connected. From Wick's theorem the product of $V\Omega^{(1)}$ could lead to disconnected diagrams. However, since $PV\Omega^{(1)}P$ must be *closed*, all of the Goldstone diagrams for $H_{eff}^{(2)}$ must be *connected.* The resulting Goldstone diagrams for $H_{eff}^{(2)}$ are shown in Fig. 13.7 of Lindgren and Morrison (1982, p298).

(iii) **Linked diagram theorem** If one part of a disconnected diagram is closed (no other free lines than valence lines for open shells) and another part is open (some free lines are core or virtual lines), such a disconnected diagram is defined to be *unlinked.* If two disconnected parts are both open, such a disconnected diagram is still *linked.* A connected diagram is always a linked diagram. The second-order wave operator $\Omega^{(2)}$ satisfies the second-order Bloch equation,

$$[\Omega^{(2)}, H_0]P = QV\Omega^{(1)}P - \Omega^{(1)}PVP.$$

It has been proved (see Lindgren and Morrison 1982) that the unlinked diagrams $(QV\Omega^{(1)}P)_{unlinked}$ from the first term are cancelled exactly by the unlinked diagrams $(\Omega^{(1)}PVP)_{unlinked}$ from the second term. Such cancellation of the unlinked diagrams in the wave operators occurs in any order, i.e. all of the

wave operators are *linked.* This is the *(full) linked diagram theorem.*

Furthermore, it can be proved that after the cancellation of the unlinked diagrams for wave operators the second-order Bloch equation can be rewritten as:

$$[\Omega^{(2)}, H_0] = Q\{V_{op}\Omega^{(1)}\}_{disconne} + Q\{\widehat{V\Omega^{(1)}}\}_{conne} - \{\Omega^{(1)}\widehat{V_{closed}}\}_{folded}. \qquad (2.17)$$

This involves three terms that all corresponding to linked diagrams. Some discussions about the derivation of this equation will be given in section 2.2. The first term corresponds to diagrams that are disconnected (V_{op} and $\Omega^{(1)}$ have no contraction) but linked (both V_{op} and $\Omega^{(1)}$ are open diagrams), the second term to connected diagrams, and the third term to the so-called *folded* or *backwards* diagrams. The linked diagram theorem leads to an important result for the effective Hamiltonian H_{eff}. Since $H_{eff}^{(n)} = PV\Omega^{(n-1)}P$, all of the free lines (other than valence lines) of $\Omega^{(n-1)}$ will be closed by V, and $PV\Omega^{(n-1)}P$ forms the closed diagrams. Even if the $\Omega^{(n-1)}$ is disconnected, after the closure on the upper lines of $\Omega_{discon}^{(n-1)}$ by V, the diagrams corresponding to $PV(\Omega^{(n-1)}P)_{discon}$ are *connected* since V is always connected. Hence *all the Goldstone diagrams of the effective Hamiltonian in any order are connected if the linked (wave-operator) diagram theorem holds.* Further discussion about this linked diagram theorem will be given in the next section.

In this way, and according to the above mentioned theorems, the wave operator $\Omega^{(n-1)}$ and the effective Hamiltonian $H_{eff}^{(n)}$ for the open shell can be constructed graphically order by order, but in fact they hardly go beyond the third order. In the case of the third-order effective Hamiltonian $H_{eff}^{(3)}$, we need to construct the second-order wave operator $\Omega^{(2)}$ first. According to equation (2.17) there are three kinds of linked diagrams of $\Omega^{(2)}$; disconnected, connected, and folded. There are 132 connected and 18 disconnected diagrams for $\Omega^{(2)}$ (Lindgren and Morrison 1982, p310). Ng and Newman (1985) have listed all of effective Hamiltonian up to third-order. As discussed above, all of the diagrams for H_{eff} are *connected* according to the linked diagram theorem.

2.2 Full linked diagram theorem and disconnected diagrams for effective Hamiltonian

According to the linked diagram theorem, all of the Goldstone diagrams for the effective Hamiltonian are connected (Lindgren and Morrison (1982) pp273, 298, 383). The

unlinked wave-operator, and so the disconnected diagrams of the effective Hamiltonian are said to be *unphysical.* This has the important implication that if the first-order perturbation operators are one-body operators only (i.e. the two-body diagrams in V (Fig. 2.1) are disregarded), in any higher order, the effective Hamiltonian is still the one-body interaction. However, in practice sometimes (such as Judd and Pooler (1982), Downer *et al.* (1988), Burdick *et al.* (1989)) an effective two-body operator in third-order such as $\sum \mathbf{W}_i^{(1,1)0}\mathbf{U}_j^{(\lambda)}$ is derived from three first-order one-body operators: spin-orbit, crystal field, and the electric dipole operators (matter-field interaction in length gauge). Such an effective operator $\sum \mathbf{W}_i^{(1,1)0}\mathbf{U}_j^{(\lambda)}$ can be identified as a disconnected Hamiltonian operator as shown in Fig. 2.4. It is an open question at this stage why Judd and Pooler (1982), Downer *et al.* (1988), Burdick *et al.* (1989) incorporate this term in apparent contradiction of the linked diagram theorem of Lindgren and Morrison (1982) and Brandow (1966,1967).

There are some differences in the content of various *linked cluster theorems*, which in some contexts mean the cancellation of the "vacuum fluctuation" diagrams, and in other the full cancellation of the "unlinked valence diagrams" such as Fig. 2.4 in addition to the "vacuum fluctuations" (see e.g. Brandow 1975). We may call the latter as a *full* linked diagram theorem, and the theorems of Brandow (1967) and Lindgren (1974) are of this kind.

In Lindgren and Morrison's book (1982 p383) they state: *"Unlinked diagram are 'unphysical' in the sense that their energy contribution increases nonlinearly with the size of the system. An unlinked energy diagram for a closed-shell system can be separated into two or more diagram parts, each of which is an allowed (linked) energy diagram. In each such part there is an independent summation over all electrons of the system. For a system of noninteracting atoms this would lead to 'cross-terms', where different parts of the diagram refer to different atoms. Obviously, such nonlinear terms have no physical relevance: and, in particular, they can cause a considerable error in calculations of quantities like dissociation energies. Such nonlinear effects are retained in truncated configuration interaction (CI), while they are eliminated in linked-diagram expansion (LDE)."* The disconnected diagram Fig. 2.4 does have two independent parts and the summation should run over all of the electrons for each part although in the original papers of Judd, Downer, and Burdick the summation is not explicit. Hence such diagram seems to be "unphysical" since it has a "cross-term" according to Lindgren and Morrison.

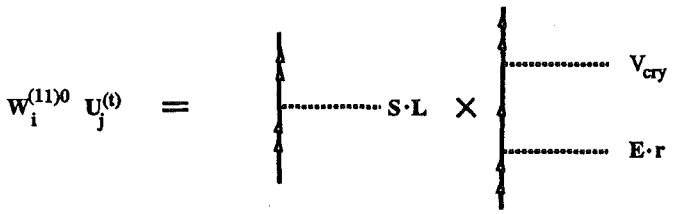


Figure 2.4 The effective operator $\sum W_i^{(1,1)0} U_j^{(\lambda)}$ in terms of the Goldstone diagram

Brandow (1975) said at a conference: *"There is no discussion (in Sandars' paper (1969)) of the existence or nonexistence of unlinked valence diagrams such as (4.2) (a similar diagram to Fig. 2.4 here). In common with some other authors, he (Sandars) uses the term 'linked' to mean simply the absence of 'vacuum fluctuations', thus (4.2) would be described as 'linked but disconnected'. ··· The first correct diagrammatic representation for the result (4.8) was given in Ref.1 (Brandow 1967), ··· The topological properties and diagrammatic rules for the folded diagrams were spelled out in full detail, and a general proof was given for the cancellation of unlinked valence diagrams (such as (4.2) or Fig. 2.4 here). ··· There are several reasons why it is nice to have a fully linked result. There is the practical matter of having far fewer diagrams to calculate. Formally, this leads to much more straightforward physical interpretation. And in cases where there are a large number of valence particles, it saves one from the sort of pathology found in the unlinked BW treatment of the closed-shell problem – denominators spuriously large because they contain the energy shift ΔE which is proportional to the number of particles."*

Lindgren and Morrison (1982, p270) also discussed that the complete cancellation of the unlinked diagrams must require *disregarding the exclusion principle* in the wave-operators. The reason for this may be explained as in the following example which is slightly different from that of Lindgren and Morrison (1982). According to Wick's theorem (eq. 2.16) the second-order Bloch equation (eq. 2.5) can be written as

$$[\Omega^{(2)}, H_0]P = Q\{V\Omega^{(1)}\}P + Q\{\widehat{V\Omega^{(1)}}\}P - \{\Omega^{(1)}PVP\} - \{\widehat{\Omega^{(1)}PVP}\}, \qquad (2.18)$$

where the first and third terms are represented by disconnected diagrams (no connection between $\Omega^{(1)}$ and V), while the second and fourth are connected. The third term (disconnected), furthermore, is unlinked since the PVP part is closed and Ω is always open. The operator V can also be written as two parts, the closed and open

parts $V = V_{cl} + V_{op}$, and $PVP = H_{eff}^{(1)}$. Then the above equation can be rewritten as

$$[\Omega^{(2)}, H_0]P = Q\{V_{op}\Omega^{(1)}\}P + Q\{V_{cl}\Omega^{(1)}\}P + Q\{V_{op}\widehat{\Omega^{(1)}}\}P - \{\Omega^{(1)}H_{eff}^{(1)}\} - \{\Omega^{(1)}\widehat{H_{eff}^{(1)}}\}. \tag{2.19}$$

In this case the second term corresponds to unlinked diagrams and it will cancel the unlinked diagrams in the fourth term. However, if we suppose that each operator is a one-body operator only (for simplicity), for the term $-\{\Omega^{(1)}H_{eff}^{(1)}\}$ the summations over the electrons can run independently but the term $Q\{V_{cl}\Omega^{(1)}\}P$ cannot because of the *exclusion principle.* Therefore in order to achieve a complete cancellation of the unlinked diagrams one must *disregard the exclusion principle*, and thus equation (2.17) in the last section is verified.

Stedman (1990) gives a different emphasis to the linked diagram theorem by using time-ordered Green's function formalism in the context of the Abrikosov projection approach to the description of ionic energy levels. He also pointed out: *"The linked cluster theorem fails under Abrikosov projection. However, the disconnected diagrams appear only in a denominator which does not affect the energy dependence and so the form of the spectral density $\rho_i(E)$".*

Can the disconnected Hamiltonian diagrams (unlinked valence diagrams) really survive in diagrammatic perturbation theory? According to Brandow, Lindgren and Morrison, and Stedman the answer would appear to be no.

Recently, Burdick and Reid (1993) have also reached the conclusion that including an "unlinked" diagram (Fig. 2.4) violates the full linked diagram theorem. Their quantitative result show that by excluding the "unlinked" diagram (Fig. 2.4) improved agreement with experiment can be obtained by including various linked two-body diagrams corresponding to electron correlation effects (i.e. including the Coulomb interaction). This has led to a discussion which continues at present.

2.3 Time-dependent perturbation theory for optical transitions in the lanthanides

Under the *valence electron excitation approximation*, in this section, we will develop a systematic diagram expansion up to third-order suitable for the even-parity optical transitions in the lanthanide ions in crystals and solutions. In this way, the one-photon and two-photon processes can be treated in the same manner, and the electron cor-

relation effect on the transition rate (i.e. a two-body Coulomb interaction between electrons is involved) can also be discussed which has not been fully investigated previously. After this systematic Feynman-type diagram perturbation analysis of the optical transitions, a Jucys-type angular momentum diagram can also be obtained if the central-field approximation is made for the zero-order Hamiltonian. By using this angular-diagram method the effective tensor operators can be derived diagrammatically. The old Judd-Ofelt (second-order) and some of Downer's (third-order) effective tensor operators can be recovered and some new operators are revealed.

The transition process is described by a time-dependent Schrödinger equation

$$i\hbar\frac{d\Psi(t)}{dt} = (H_0 + V^t)\Psi(t), \tag{2.20}$$

where H_0 is the time-independent unperturbed zero-order Hamiltonian which in general includes uncoupled radiation field and the ions, and V^t is a time-dependent perturbation. Without the perturbation the system (radiation plus ions) is described by zero-order eigenfunctions Φ_n, and $H_0\Phi_n = E_n^{(0)}\Phi_n$. Following the standard treatment of time-dependent perturbation theory the transition probability $|c_{ks}|^2$ between unperturbed states k and s due to the time-dependent perturbation V^t is given by

$$c_{ks} = -\frac{i}{\hbar}\int_{-\infty}^{\infty}\langle\Phi_k|\ V^t\ |\Phi_s\rangle e^{i\omega_{ks}t}dt. \tag{2.21}$$

This leads to Fermi's Golden Rule for the transition probability

$$P_{k\to s} = \frac{2\pi}{\hbar}\ |\langle\Phi_k|\ V^t\ |\Phi_s\rangle|^2\ \delta(E_k - E_s). \tag{2.22}$$

At this point we can discuss the linkage between time-independent (Lindgren and Morrison 1982) and time-dependent perturbation theories. Such discussions have been given by Goldstone (1957) and Oberlechner *et al.* (1970). Let Φ_0 be the ground state of H_0, $H_0\Phi_0 = E_0\Phi_0$, and let Ψ_0 be the lowest eigenstate of H. When the time-dependent perturbation V^t is switched on adiabatically, according to the adiabatic theorem (Gell-Mann and Low 1951) the system's total Hamiltonian satisfies a secular equation, i.e. a time-independent Schrödinger equation of the form

$$(H_0 + V^t)\Psi_0 = (E_0 + \Delta E)\Psi_0. \tag{2.23}$$

$H'_{eff} \equiv V^tU_\alpha/\langle\Phi_0|\ U_\alpha\ |\Phi_0\rangle$ can be defined as the effective Hamiltonian in a time-dependent system and

$$\Delta E = \langle\Phi_0|\ V^t\ |\Psi_0\rangle = \lim_{\alpha\to 0}\frac{\langle\Phi_0|\ V^tU_\alpha\ |\Phi_0\rangle}{\langle\Phi_0|\ U_\alpha\ |\Phi_0\rangle}, \tag{2.24}$$

where V^t is the perturbation and U_α a time evolution operator

$$U_\alpha = \sum_{n=0}^{\infty}(-i)^n \int_{0>t_1>t_2>\cdots>t_n} V^{t_1}V^{t_2}\cdots V^{t_n}dt_1dt_2\cdots dt_n.$$

Such an effective Hamiltonian $H'_{eff} \equiv V^tU_\alpha/\langle\Phi_0|\ U_\alpha\ |\Phi_0\rangle$ only acts within the zero-order (time-independent) wavefunctions, where $U_\alpha/\langle\Phi_0|\ U_\alpha\ |\Phi_0\rangle$ plays the same role as the wave operator Ω in Lindgren and Morrison (1982)'s formalism, in which we define $H_{eff} = PV^t\Omega P$. Here the projection operator P restricts our interest to a certain subspace (the model space) of the whole Hilbert space. Then (Goldstone 1957) the required perturbation formulae for Ψ_0 and ΔE are obtained on carrying out the time integrations in the expression for the limits in equation (2.24).

Therefore in terms of the effective Hamiltonian H_{eff} in the time-independent formalism of Lindgren and Morrison (1982) we can write the transition coefficient within the model space as

$$c_{ks} = -\frac{i}{\hbar}\int_{-\infty}^{\infty}\langle\Phi_k|H_{eff}|\Phi_s\rangle e^{i\omega_{ks}t}dt; \quad k,s = 1,2,\cdots,d, \tag{2.25}$$

where H_{eff} is the effective Hamiltonian defined in section 2.1, d is the dimension of the model space, and $H_{eff} = PV^t\Omega P$ where P is a projection operator defined by eq. (2.1), $P = \sum_{n\in P}|\phi_n^{(0)}\rangle\langle\phi_n^{(0)}|$. The effective Hamiltonian H_{eff} acts within the model space only (see eqns. (2.7), (2.8), $\cdots$ (2.11)). In a perturbation expansion, by using Fermi's golden rule order by order, we have

$$\begin{aligned}
P_{ks}^{(1)} &= \frac{2\pi}{\hbar}|\langle k|\ H_{eff}^{(1)}\ |s\rangle|^2\ \delta(E_k - E_s),\\
P_{ks}^{(2)} &= \frac{2\pi}{\hbar}|\langle k|\ H_{eff}^{(2)}\ |s\rangle|^2\ \delta(E_k - E_s),\\
P_{ks}^{(3)} &= \frac{2\pi}{\hbar}|\langle k|\ H_{eff}^{(3)}\ |s\rangle|^2\ \delta(E_k - E_s),\\
&\cdots
\end{aligned}$$

where $H_{eff}^{(1)} = PV^tP$, $H_{eff}^{(2)} = PV^t\Omega^{(1)}P$, and $H_{eff}^{(3)} = PV^t\Omega^{(2)}P$. The perturbation expansion of V^t can then be treated exactly in the same manner as in section 2.1, i.e. the wave operator Ω is governed by the Bloch equation (eq. 2.2) and the entire Goldstone diagram formalism of Lindgren and Morrison (1982) can be applied. Although Lindgren and Morrison (1982)'s formalism is based on the time-independent Bloch equation, their diagram rules are designed in accord with time-dependent Goldstone rules.

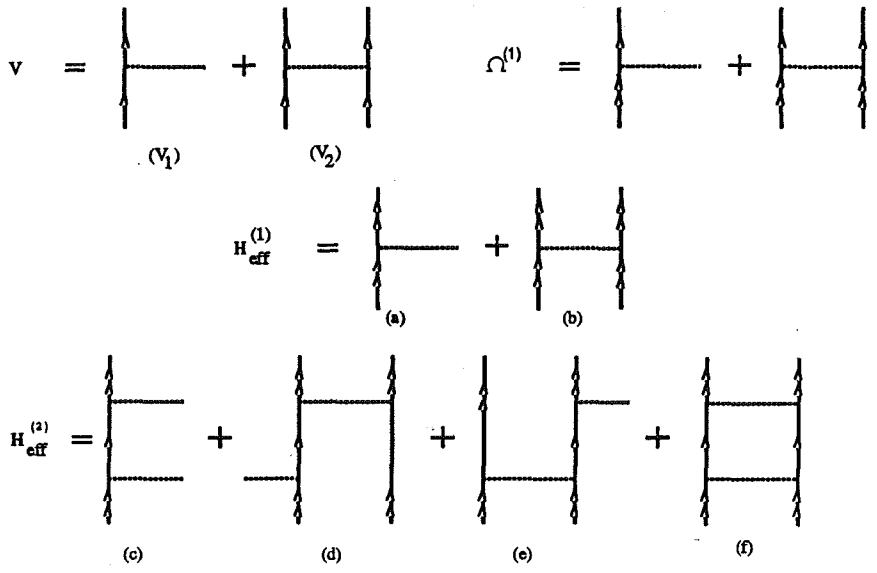


Figure 2.5 Diagrammatic representations of V, $\Omega^{(1)}$, $H_{eff}^{(1)}$, and $H_{eff}^{(2)}$.

Thus we can treat the energy level structure and transition processes on the same footing. The zero-order Hamiltonian is chosen as the Hamiltonian with the independent particle model and the central field approximation, $H_0 = \sum_{i=1}^{N}(\mathbf{p}_i^2/2m - Ze^2/r_i + u_i)$. Within the range of interest the perturbation V can be chosen as

$$V = V_1 + V_2; \quad V_2 = V_{Coulomb}, \quad V_1 = V_{SO} + V_{cry} + V^t, \tag{2.26}$$

where V_1 (V_2) refers to one-body (two-body) interaction, $V_{SO} = \lambda \mathbf{S} \cdot \mathbf{L}$ (spin-orbit interaction), V_{cry} is the crystal field, V^t contains the one-body time-dependent matter-field interaction operator(s), and V_2 is the two-body Coulomb interaction and its effective one-body part vanishes in the Hartree-Fock approximation. In a diagram a dashed line with a free end represents all the one-body interactions in which we are interested, $V_1 = V_{SO} + V_{cry} + V^t$. Hence one such dashed line with a free end may correspond to any of these different one-body interactions.

Our interest is the optical transition processes within an atomic system, in particular the optical transitions within lanthanide ions in crystals or solutions. In these cases, since the core electron optical excitation is much more difficult than valence electron excitations, we make the approximation that *only valence electrons may be excited (by interaction with electromagnetic field).* When core excitations are ignored, the number of the diagrams will be greatly reduced. For the lanthanide ion case, the

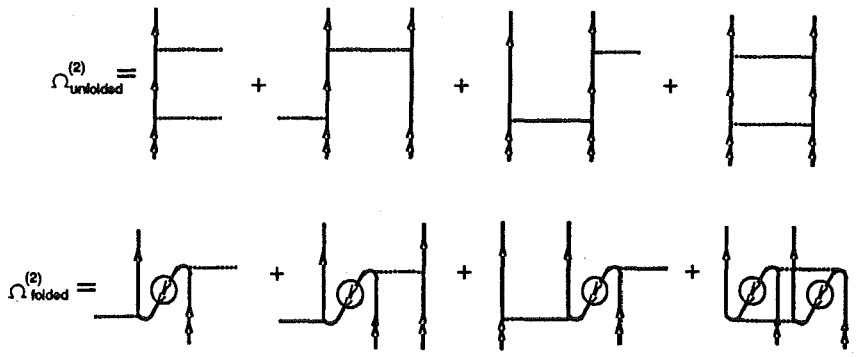


Figure 2.6 Diagrammatic representations of second-order wave operators $\Omega^{(2)}_{unfolded}$ and $\Omega^{(2)}_{folded}$.

model space can then be chosen as the valence configuration $4f$ only, and the optical transition processes will be restricted to be the intra-configuration even parity transitions. For inter-configuration optical transitions the model space has to be enlarged to involve at least two configurations which will not be discussed in this chapter. In this way, the Goldstone diagrams for $V = V_1 + V_2$ are the diagrams with no downward lines in Fig. 2.1. There are only two diagrams which satisfy this requirement: denoted as (V_1) and (V_2) in Fig. 2.5.

The diagrams for $\Omega^{(1)}$ come from eq. (2.4), $[\Omega^{(1)}, H_0]P = QVP$, the first order Bloch equation. Hence the diagrams for $\Omega^{(1)}$ are the same as the diagrams for V except that there are no particle lines below the interaction vertices apart from the valence (double arrow) lines. Thus the difference between V and $\Omega^{(1)}$ is only that the incoming particle lines for $\Omega^{(1)}$ are the valence electrons (double arrow), and for V are the virtual and valence electrons (single upgoing arrow).

For first-order effective Hamiltonian, we have $H^{(1)}_{eff} = PVP$. This tells us directly that the Goldstone diagrams for $H^{(1)}_{eff}$ are the closed diagrams of V, i.e. both the incoming and the outgoing particle lines are the valence lines. Such an effective Hamiltonian acts within the model space. Up to this point all first-order diagrams have obtained, and they are the basis for forming higher order diagrams.

The second-order effective Hamiltonian is $H^{(2)}_{eff} = PV\Omega^{(1)}P$. The Goldstone diagrams for it are the graphical product of V and $\Omega^{(1)}$, and they are *closed* by P. In performing this product Wick's theorem and the closed diagram rule must be applied. In section 2.1 the related problems of applying these two theorems have been discussed. According to Lindgren and Morrison (1982) the Goldstone diagrams

for $H_{eff}^{(2)} = PV\Omega^{(1)}P$ are all connected. Following Lindgren and Morrison (1982) we can simply collect the Goldstone diagrams which satisfy the condition of having no downward lines in Fig. 13.7 of Lindgren and Morrison (1982) for one-body and two-body diagrams, and they are collected in Fig. 2.5 from (c) to (f).

The diagrams corresponding to the third-order effective Hamiltonian $H_{eff}^{(3)}$ are obtained from the equations

$$H_{eff}^{(3)} = PV\Omega^{(2)}P, \tag{2.27}$$

$$[\Omega^{(2)}, H_0]P = (QV\Omega^{(1)}P - \Omega^{(1)}PVP)_{linked}. \tag{2.28}$$

According to eq. (2.17) the first term of eq. (2.28) will give all the linked and unfolded diagrams of $\Omega^{(2)}$, and the second term gives the so-called *folded diagrams.* These second-order wave operators $\Omega_{unfolded}^{(2)}$ and $\Omega_{folded}^{(2)}$ are listed in Fig. 2.6. Thus eq. (2.27) can be written as

$$H_{eff}^{(3)} = PV\Omega_{unfolded}^{(2)}P + PV\Omega_{folded}^{(2)}P \tag{2.29}$$

All unfolded diagrams in the third-order effective Hamiltonian are presented in Fig. 2.7, and folded diagrams in Fig. 2.8. Evidently, in third-order, there are only 17 diagrams to be concerned and this is a manageable number of diagrams. Here we have applied the fully linked diagram theorem (Brandow 1967 and Lindgren 1974). This means that the disconnected diagrams such as Fig. 2.4 cancel.

For optical transition processes we will restrict ourselves to the length gauge and the E1 approximation only in this chapter, and this means that we have the time-dependent perturbation $V^t = H_E + H_S' = -e\mathbf{E}\cdot\mathbf{r} + e\mathbf{E}\cdot\mathbf{s}\times\mathbf{p}/2m^2c^2$ where H_E is the E1 interaction and H_S' is a new spin-dependent matter-field interaction discussed by Wang and Stedman (1993) (see also chapter 6). In this length gauge the spin-dependent matter-field interaction $H_T = -e\lambda\mathbf{A}\cdot\mathbf{S}\times\mathbf{r}$ is cancelled exactly in first-order (see Drake (1972, 1976), or eq. 6.13 of chapter 6). H_E and H_S' are odd-parity one-body interactions and correspond to the Goldstone diagram (a) in Fig. 2.5. In first-order perturbation (see diagram (a) and (b) in Fig. 2.5) the optical transition processes are governed by the matter-field interaction operators V^t which are time-dependent, and the use of $H_{eff}^{(1)} = PV^tP$ means that we only consider the optical transitions within the model space which itself is chosen according to the physical problem. For lanthanides, this model space can be chosen as the $4f^N$ configuration. According to the parity selection rule H_E and H_S' cannot have a non-zero matrix

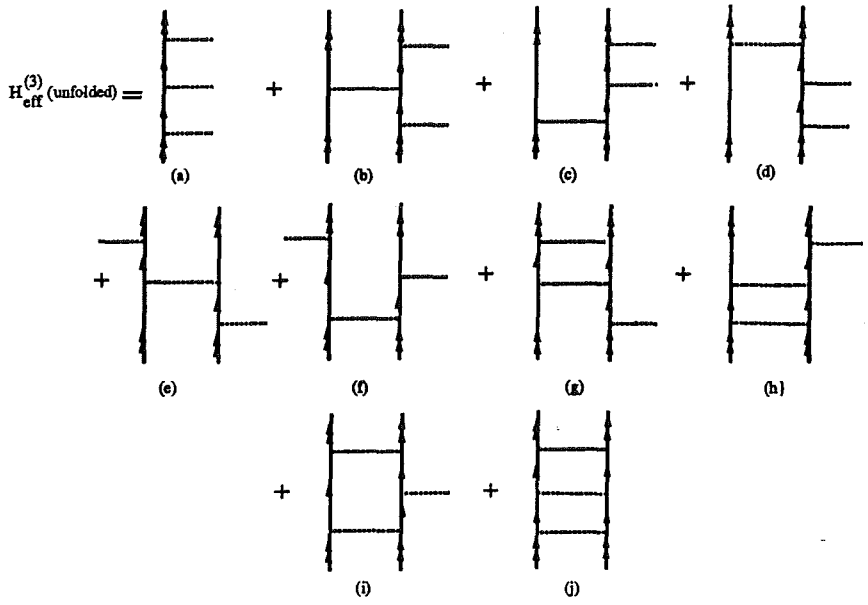


Figure 2.7 Unfolded third-order diagrams of $H_{eff}^{(3)}$.

element within this model space. Even-parity matter-field interactions such as the Zeeman term which are distinguished as magnetic dipole (M1) terms are excluded from consideration.

In nth-order perturbation there are n interactions corresponding to n dashed lines in a Goldstone diagram. For a one-photon optical transition process one matter-field interaction H_E or H'_S must be included in these n interactions, and the other interactions are intra-atomic. Likewise, for two-photon processes two matter-field interactions, two H_E, or one H_E plus one H'_S, or two H'_S, must be involved in a diagram.

2.4 Goldstone diagrams for even-parity intra-configuration optical transitions

Now we can analyse the optical transition processes within the model space in a systematic way. After making the valence electron excitation approximation, and including from first-order to third-order perturbations, $H_{eff}^{(1)} + H_{eff}^{(2)} + H_{eff}^{(3)}$, we obtain altogether 23 Goldstone diagrams as in Figs. 2.5, 2.7, and 2.8. From parity considerations, the total parity of interactions involved in a diagram term must be *even* since the model space here is chosen as the $4f^N$ configuration for lanthanides,

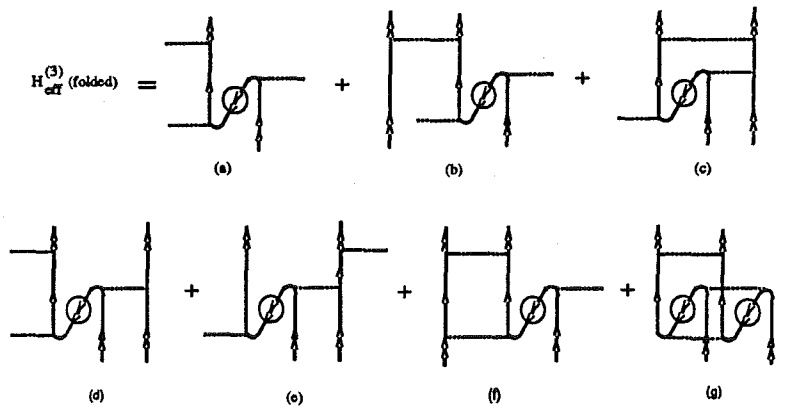


Figure 2.8 Third-order folded diagrams of $H_{eff}^{(3)}$.

and these valence diagrams represent the intra-configurational processes. At least one matter-field one-body interaction must be included because we are dealing with optical transitions. Only 9 out of 23 diagrams, those listed in Fig. 2.9, satisfy such requirements. These nine diagrams can be applied to both one-photon and two-photon processes while in Fig. 2.9 we only denote one possible two-photon process for each diagram. The two-photon processes include two-photon absorption, and Raman and Rayleigh scattering. Since our one-body perturbation V_1 is $H_E + H'_S + V_{SO} + V_{cry}$, each dashed line with a free end can be interpreted as four different interactions which in fact correspond to four different diagrams. We do not distinguish these for the sake of simplicity. Hence a particular one-body interaction in Fig. 2.9 can be replaced by another one-body term provided that they have the same parity; one H_E can be replaced by either H'_S or an odd-parity crystal field $V_{cry}^{(o)}$. For the one-photon process the Goldstone diagrams have only one one-body matter-field interaction line, either H_E or H'_S. For the two-photon process there are two matter-field interaction lines corresponding to two H_E, or one H_E and one H'_S, or two H'_S. Any diagram involving either H'_S or V_{SO} is a spin-dependent diagram.

We can see that in first-order perturbation the E1 intra-configuration optical transitions cannot be produced, and the permitted first-order effective Hamiltonian is the energy splitting terms, $H_{eff}^{(1)} = V_{Coulomb} + V_{SO} + V_{cry}^{e}$ which are all even parity. For the purpose of the energy level splittings they could be sufficient in first order. The "core polarization" (omitted in our consideration) and the second-order Coulomb terms may be the candidates for the fine structure of the energy levels.

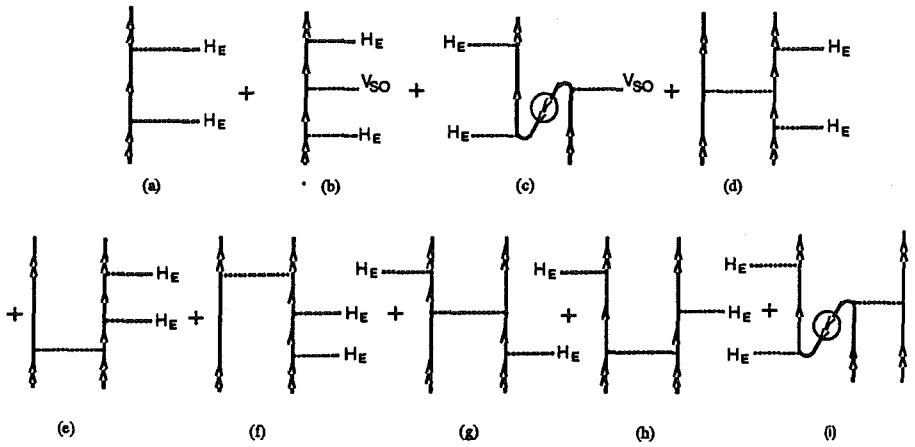


Figure 2.9 Goldstone diagrams for optical transitions in the lanthanides up to the third-order perturbation.

The even parity matter-field coupling is permitted in second-order perturbation at lowest order. For the one-photon process it corresponds to the Judd-Ofelt theory, and it can also be used for two-photon processes. Such a diagram ((a) in Fig. 2.9) is an effective one-body interaction. The Coulomb interaction cannot assist the optical transition up to the second-order.

The third-order diagrams are (b) – (i) in Fig. 2.9. Among them (b) and (c) are the one-body interactions which involve three first-order one-body terms, H_E (or H'_S), V_{SO}, and another H_E (or H'_S) for two-photon processes (or a $V^{(o)}_{cry}$ for one-photon process). We can see that only these two third-order diagrams can involve spin-orbit interaction. Thus they correspond to the third-order mechanism discussed by Downer *et al.* (1988) for the two-photon and the one-photon processes if only electric dipole H_E is concerned. The difference is that they disregarded the full linked diagram theorem and obtained a disconnected Hamiltonian (Fig. 2.4) which is referred to as unlinked here. The diagram (c) is a folded diagram in which a downward line with a circle and a double arrow denotes the valence orbital. In this diagram (c) the spin-orbit interaction can only act within the ground (valence) configuration $4f^N$, $V_{SO} = \zeta_f \mathbf{S} \cdot \mathbf{L}$, while the diagram (b) can have the spin-orbit interaction within the excited configuration $5d$ for example, and $V_{SO} = \zeta_d \mathbf{S} \cdot \mathbf{L}$. Since the folded diagrams come from the second term of eq. (2.28), diagram (c) has an opposite sign to the unfolded diagram (b). It is interesting to note that some terms in the results of Downer *et al.* (1988) have the same effect, namely the terms proportional to $(\zeta_f - \zeta_d)$, even though they did

not have a folded diagram. Burdick and Reid (1993) also independently obtained the same diagrammatic results as Fig. 2.9, and diagrams (b) and (c) correspond to their equations (2) and (3).

The diagrams (d) – (i) in Fig. 2.9 are all two-body interactions, in which a Coulomb interaction is involved, i.e. the Coulomb interaction may assist the optical transitions in third-order perturbation as the lowest order. The electrons correlate each other while the transition occurs. This electron correlation effect has been discussed by Smentek-Mielczarek (1991,1992) to some extent for electronic Raman scattering, the one-photon and two-photon absorptions.

We note that the spin-orbit interaction cannot be included either in these third-order effective two-body diagrams (d) – (i) or in second-order one-body diagram (a) in Fig. 2.9 since V_{SO} has even parity. That means diagrams (b) and (c) are the only two diagrams in Fig. 2.9 which can accommodate the spin-orbit interaction V_{SO}. If we disregard H'_S (a new operator which has not been noted before our work) all other transition diagrams are spin-independent. However, H_E can be replaced by H'_S and the resulting two-body diagrams will be spin-dependent effective one-body or two-body matter-field interactions.

In principle, we can also discuss the inter-configurational optical transitions in the same manner. But in that case, one has to enlarge the model space to involve at least two configurations with opposite parity. Of course the corresponding parity selection rules have to be altered. Such inter-configuration transition is not our main interest in this thesis.

In summary, the Goldstone diagram perturbation theory provides us a means of investigating all optical transition processes in a systematic and coherent way. Up to third-order, only nine diagrams accommodate all of previous known theories of the one-photon absorption, two-photon absorption, Raman, and Rayleigh scatterings. The new effective two-body transition operators are presented in third-order.

Furthermore, such a diagram analysis has another important advantage; it also provides the ground for a Jucys-type angular momentum diagram analysis since the angular part can be separated out from the interaction if the *central field approximation* is used for the system zero-order Hamiltonian. This central field approximation is the basis of using a group chain $U_{4l+2} \rightarrow SU_2 \times SO_3$ to describe the atomic (or nuclear) bounded system initiated by Racah (1949). An $SU_2 \times SO_3$ angular diagram analysis will lead to the *effective tensor operators* discussed in next section.

2.5 Angular diagrams and effective tensor operators

In the Goldstone diagrams each vertex represents an interaction with *one particle* only. However, in practice there may be N electrons in the same configuration (e.g. $4f^N$) and the angular momenta of these electrons are coupled together, the translation from the Goldstone diagram to the angular diagram is a little more complicated. Now we choose the simplest case, second-order Judd-Ofelt theory (Judd 1962, Ofelt 1962) i.e. diagram (a) of Fig. 2.9, as an example to investigate and establish an angular-diagram method of the derivation of the effective tensor operators. In chapter 5, a full discussion about the even-rank rule obtained by Judd and Ofelt and the comparison with the time reversal selection rules will be given. Here we focus our attention on the linkage between the Goldstone diagram and the Jucys-type angular diagram and a simplified angular diagram method to derive the angular part in terms of the effective tensor operators.

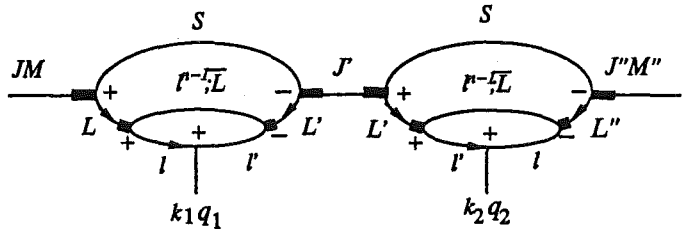
The matrix elements in the Judd-Ofelt second-order perturbation contribution to intensities can be written as

$$\sum[\frac{1}{\Delta E}\langle l^N\alpha SLJM_J|H_E^{(k_1)}|l^{N-1}l'\alpha'SL'J'M'_J\rangle\langle l^{N-1}l'\alpha'SL'J'M'_J|V_{cry}^{(k_2)}|l^N\alpha''SL''J''M''_J\rangle + \frac{1}{\Delta E-\hbar\omega}(H_E^{(k_1)}\leftrightarrow V_{cry}^{(k_2)})] \simeq \sum\frac{1}{\Delta E}\,[\,\mathcal{M}+\mathcal{N}\,], \tag{2.30}$$

where $\mathcal{M}$ and $\mathcal{N}$ are abbreviations for the first and the second numerators, and the summation should run over all of intermediate states $|l^{N-1}l'\alpha'SL'J'M'_J\rangle$, and k_1 and k_2. Normally it is noted that the condition $\hbar\omega \ll \Delta E$ is well satisfied, and it leads to a good approximation to the right-hand-side of the above equation. More precisely (see Moore and Stedman 1990) the formula $\frac{\mathcal{M}}{\Delta E}+\frac{\mathcal{N}}{\Delta E-\hbar\omega}$ can be written as the symmetrised part $\frac{1}{2}(\frac{1}{\Delta E}+\frac{1}{\Delta E-\hbar\omega})(\mathcal{M}+\mathcal{N})$ plus the antisymmetrised part $\frac{1}{2}(\frac{1}{\Delta E}-\frac{1}{\Delta E-\hbar\omega})(\mathcal{M}-\mathcal{N})$. The above approximation is the symmetrised part only. The effects of the antisymmetrised part will be discussed in chapter 5. The states here are written in the Russell-Saunders coupling (LS-coupling) scheme of the N-electron states, e.g. $|l^N\alpha SLJM_J\rangle$. Since the one-body interactions $H_E^{(k_1)}$ and $V_{cry}^{(k_2)}$ act within the one-particle state only, the N-electron state must be factorised into an *(N-1)*-particle state and a one-particle state with an appropriate *fractional parentage coefficient* (cfp). Besides, the states written in this way (Russell-Saunders coupling) mean that a central field approximation for the zero-order Hamiltonian of the atomic system has been made. The matrix element can be separated as a radial integral

part, a reduced orbital part, and an angular part. Each angular momentum coupling in SO_3 is represented by a 3jm symbol with appropriate phase. Thus the first term $\sum \frac{\mathcal{M}}{\Delta E}$ of eq. (2.30) can be written as

$$\sum \frac{\mathcal{M}}{\Delta E} = \sum \frac{1}{\Delta E}$$



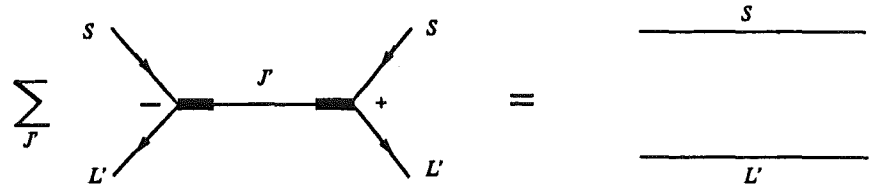
$$\times\ (l^N L\{|l^{N-1}\bar{L}, l)(l^{N-1}\bar{L}'', l|\}l^N L'')\ (nl|r^{k_1}|n'l')(nl|r^{k_2}|n'l')(l||C^{(k_1)}||l')(l'||C^{(k_2)}||l). \tag{2.31}$$

Here the radial integral part is $(nl|r^{k_1}|n'l')(nl|r^{k_2}|n'l')$, the reduced orbital part is written as $(l||C^{(k_1)}||l')(l'||C^{(k_2)}||l)$, and the angular part is denoted by an angular-diagram associated with appropriate $cfps$ denoted as $(l^N L\{|l^{N-1}\bar{L}, l)(l^{N-1}\bar{L}'', l|\}l^N L'')$. The Jucys-type angular momentum coupling diagram (SO_3) is used, and the phase conventions (arrows, $+/-$ signs) are in agreement with Lindgren and Morrison (1982). Each dark bar in the diagram denotes a normalization factor such as $[J]^{1/2} \equiv (2J+1)^{1/2}$. We can see that the angular diagram is not simply topologically identical to the corresponding Goldstone diagram (a) in Fig. 2.9. The complication is due to the many-particle coupling. Calculating this matrix element involves all of the intermediate and unknown quantum numbers $n'l'$, L', J', and M'_J. Judd and Ofelt (1962) introduced the *effective tensor operator* which only acts between the initial state $\langle l^N \alpha S L J M_J|$ and the final state $|l^N \alpha'' S L'' J'' M''_J\rangle$ which are in the same ground configuration nl^N. By doing so one has to introduce the *closure approximation* and in return can eliminate the intermediate quantum numbers L', J', and M'_J and be left with only the angular quantum number l' of the excited configuration.

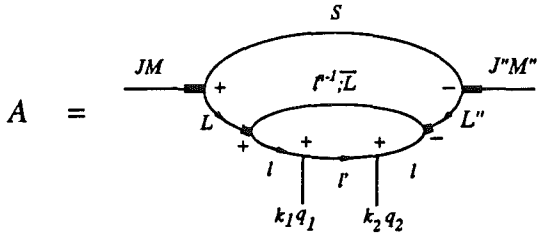
Here we will use the angular-diagram method, in particular the JLV theorems (Jucys *et al.* (1960), Stedman (1990)), to re-derive Judd-Ofelt effective tensor operator with the purpose of establishing a standard diagram method of deriving the effective tensor operators for any Goldstone diagrams.

It is understood that the summation in eq. (2.31) should run over all of the states $n'l'$, L', J' and M'_J. In general, the energy is different for each these intermediate quantum numbers. However the energy differences among these L', J' and M'_J are much smaller than the energy separation of two configurations nl^N and $n'l'$. Hence

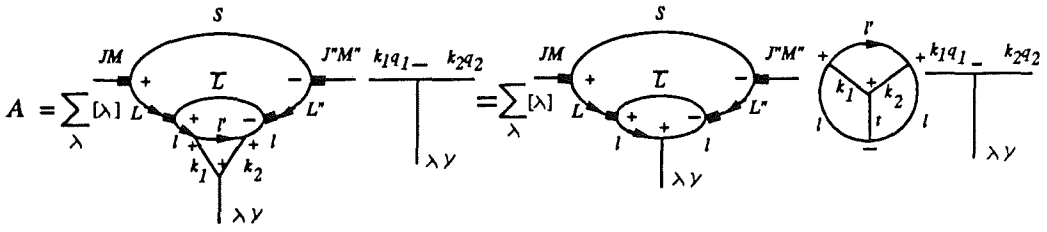
Judd and Ofelt introduce the "closure approximation", i.e. suppose that all of L', J' and M'_J are degenerate. Under this approximation the orthogonality relation is satisfied. Hence for the J' line we have



where these lines are internal lines of an angular-diagram and the quantum numbers M_S, M'_L and M'_J have been summed over. For the L' line the same rule is also applied and the angular part of eq. (2.31) can be rewritten as A,



Thus L', J' and M'_J disappear from the diagram. The next step is to apply the unitarity of the 3jm symbols which can be used to "pinch" the k_1 and k_2 lines and to form a λ line. Applying JLV3 for two l lines and a λ line, thus a 6j symbol can be separated out. We obtain



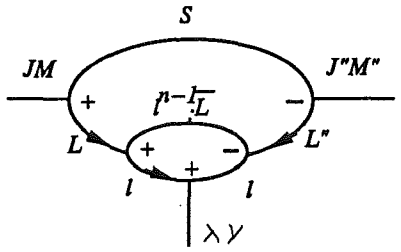
Translating the angular-diagrams into the normal nj symbols, the first diagram on the right-hand-side is a $9j$ symbol with a 3jm symbol, or equivalently two $6j$ symbols with a 3jm symbol as be explained by eq. 2.34; the second diagram is a $6j$ symbol; and the last one is a 3jm symbol. The eq. (2.31) can then be rewritten as

$$\begin{aligned}\sum \frac{\mathcal{M}}{\Delta E} &= \sum \frac{1}{\Delta E}(nl|r^{k_1}|n'l')(nl|r^{k_2}|n'l')(l||C^{(k_1)}||l')(l'||C^{(k_2)}||l) \\ &\times \sum_\lambda [\lambda](-1)^{k_1+k_2} \begin{Bmatrix} k_1 & k_2 & \lambda \\ l & l & l' \end{Bmatrix} \begin{pmatrix} k_1 & \lambda & k_2 \\ q_1 & -\gamma & q_2 \end{pmatrix} \\ &\times \langle l^N \alpha S L J M_J | U^{(\lambda)}_\gamma | l^N \alpha'' S L'' J'' M''_J \rangle . \end{aligned} \tag{2.32}$$

This result is in agreement with Judd (1962) and Ofelt (1962). Here the matrix element of the effective tensor operator $U_\gamma^{(\lambda)}$ is defined as

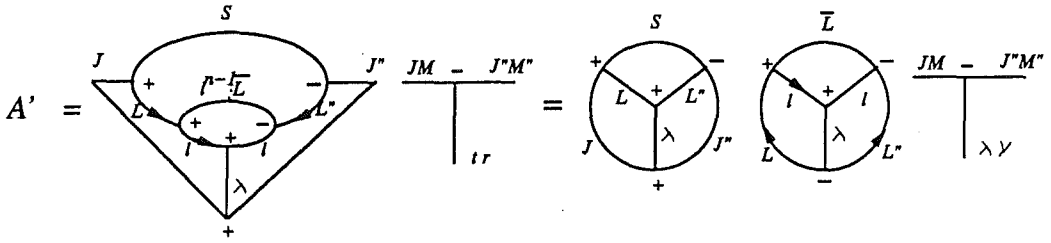
$$\langle l^N \alpha S L J M_J | U_\gamma^{(\lambda)} | l^N \alpha'' S'' L'' J'' M_J'' \rangle$$
$$= [L, J, L'', J'']^{1/2} \sum_{\bar{L}} (l^N L \{| l^{N-1} \bar{L}, l)(l^{N-1} \bar{L}'', l | \} l^N L'') \times A' \qquad (2.33)$$

$A' =$



Translating the angular-diagram A' into the nj symbols one can apply the JLV3 for three free lines, J, λ, and J''. This leads to a $9j$ symbol with a 3jm symbol. Then applying JLV3 for L, λ, and L'' lines a $6j$ symbol is separated out, and it leads to two $6j$ symbols with a 3jm symbol.

$A' =$



Thus we have

$$\langle l^N \alpha S L J M_J | U_\gamma^{(\lambda)} | l^N \alpha'' S'' L'' J'' M_J'' \rangle$$
$$= [L, J, L'', J'']^{1/2} \sum_{\bar{L}} (l^N L \{| l^{N-1} \bar{L}, l)(l^{N-1} \bar{L}'', l | \} l^N L'')(-1)^{2S+L+L''+J''+\lambda}$$
$$\times \begin{Bmatrix} J & J'' & \lambda \\ L'' & L & S \end{Bmatrix} \begin{Bmatrix} L & L'' & \lambda \\ l & l & \bar{L} \end{Bmatrix} \begin{pmatrix} J & \lambda & J'' \\ M_J & -\gamma & M_J'' \end{pmatrix}. \qquad (2.34)$$

This result (eq. 2.34) is the same as that of Ofelt (1962) who gave an explicit expression of the matrix element of the effective tensor operator $U_\gamma^{(\lambda)}$.

Applying the same approach for the second term $\sum \frac{\mathcal{N}}{\Delta E}$ in eq. (2.30), a similar result is obtained with the ranks k_1 and k_2 swapped. Finally, the even-rank rule obtained by Judd and Ofelt can be verified. Detailed discussion about this rule is given in section 5.2 of chapter 5.

2.6 Effective tensor operators derived by angular diagram method from Goldstone diagrams

In the last section we have demonstrated the power and the equivalence of the angular-diagram method for the purpose of deriving the effective tensor operators for second-order perturbation. Such an approach is still somewhat complicated.

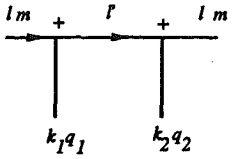
Here we attempt to give another simplified approach of deriving such effective tensor operators for any Goldstone perturbation diagram. The complication of the above derivations is mainly due to the presence of many-particle states. In fact, the associated coupling is presented only in the matrix element of the effective tensor operator $U_\gamma^{(\lambda)}$ (eq. (2.34) or the angular-diagram A'), and such an effective operator may be the same for different perturbation terms. In practice, the different perturbation terms may have the similar effective tensor operators (with different ranks) if they have the same spin-dependence and the same n-body interaction. For different spin-dependence and different n-body interaction, different (effective) tensor operators and their matrix elements have been well defined, such as $W_{\rho,q}^{(\kappa,k)}$ for spin-dependent one-body tensor operator, or $\sum_{i\neq j} U_i^{(k_1)} U_j^{(k_2)}$ for spin-independent two-body tensor operator, etc. Hence this many-particle state coupling may be an unnecessary complication, and can be avoided in the following approach.

For Judd-Ofelt second-order one-photon absorption the Goldstone diagram (a) of Fig. 2.9, according to the standard approach of second quantisation (see Lindgren and Morrison 1982), can be evaluated as

$$\sum a_l^\dagger a_l [\frac{\langle l|H_E^{(k_1)}|l'\rangle\langle l'|V_{cry}^{(k_2)}|l\rangle}{\Delta E} + \frac{\langle l|V_{cry}^{(k_2)}|l'\rangle\langle l'|H_E^{(k_1)}|l\rangle}{\Delta E'}] \simeq \sum a_l^\dagger a_l [\frac{m+n}{\Delta E}]. \qquad (2.35)$$

Here the states of the matrix elements are the one-particle states, e.g. l is the shorthand notation of $lm_l sm_s$, for the one-body interaction without worrying about the many-particle coupling. Because of the central field approximation, it can also be separated as a radial integral part, a reduced orbital part, and an angular part as before. The angular part is denoted by an angular-diagram which *is topologically identical* to the corresponding Goldstone diagram (a) of Fig. 2.9. For the first term of eq. (2.35) we have

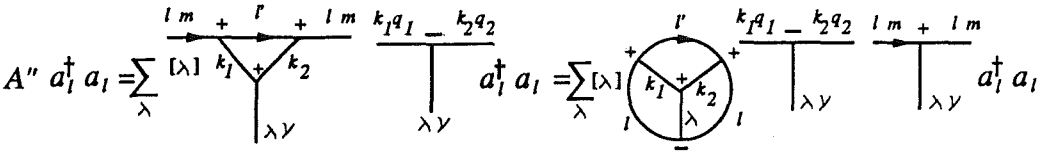
$$\sum(a_l^\dagger a_l)\frac{m}{\Delta E} = \sum(nl|r^{k_1}|n'l')(nl|r^{k_2}|n'l')(l||C^{(k_1)}||l')(l'||C^{(k_2)}||l) \times A''(a_l^\dagger a_l) \quad (2.36)$$

$A''\ \ a_l^\dagger a_l\ =$ 

$a_l^\dagger a_l$

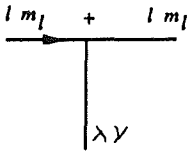
This angular-diagram A'' has the same feature as the Goldstone diagram (a) of the effective Hamiltonian $H_{eff}^{(2)}$ in Fig. 2.9; they act within the model configuration (ground configuration), and only act within one-particle states. It can be regarded as only a part of the total angular momentum coupling diagram A. Using this diagram means that the closure approximation of Judd and Ofelt has been made.

Now applying the same approach of JLV theorems we obtain

$A''\ a_l^\dagger a_l =$ 

$a_l^\dagger a_l$

Here the last diagram on the right-hand-side is a 3jm symbol;



$= \quad (-1)^{l-m_l} \begin{pmatrix} l & \lambda & l \\ -m_l & \gamma & m_l \end{pmatrix}$

Since this diagram is only a part of the total angular momentum coupling diagram, two l lines are the internal lines and m_l should be summed over. This 3jm symbol associated with the creation $a^\dagger_{lm_l sm_s}$ and annihilation $a_{lm_l sm_s}$ operators, $a_l^\dagger$ and a_l are their shorthand notations, suggests that the $a^\dagger_{lm_l sm_s}$ and $a_{lm_l sm_s}$ could be coupled together to form a (effective) tensor operator with the orbital rank λ (see for example Judd (1967)). It is known that the creation operator $a^\dagger_{lm_l sm_s}$ is a spherical tensor operator with the spin rank 1/2 and the orbital rank l, but the annihilation operator $a_{lm_l sm_s}$ is not. However a *tilded annihilation operator* (one related by a 2jm transformation)

$$\tilde{a}_{l,s,m_l,m_s} = (-1)^{l-m_l+s-m_s} a_{l,s,-m_l,-m_s}$$

is a spherical tensor operator with the spin rank 1/2 and the orbital rank l. Thus a coupled tensor of creation-annihilation pair can be defined as

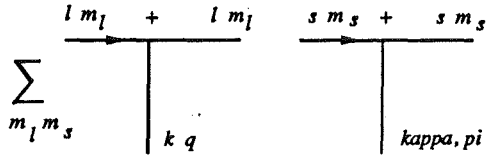
$$(\mathrm{a}^\dagger\mathrm{a})^{(\kappa,k)}_{\pi,q} = [\kappa,k]^{\frac{1}{2}} \sum_{m_l,m_s} (-1)^{q+\pi} \begin{pmatrix} l & l & k \\ m_l & m_l & -q \end{pmatrix} \begin{pmatrix} s & s & \kappa \\ m_s & m_s & -\pi \end{pmatrix} a_l^\dagger \tilde{a}_l$$

$$= [\kappa,k]^{\frac{1}{2}} \sum_{m_l,m_s} (-1)^{2l+2s} \begin{pmatrix} l & k & l \\ -m_l & q & -m_l \end{pmatrix} \begin{pmatrix} s & \kappa & s \\ -m_s & \pi & -m_s \end{pmatrix} a_l^\dagger \tilde{a}_{lm_lsm_s}$$

$$= -[\kappa,k]^{\frac{1}{2}} \sum_{m_l,m_s} \begin{pmatrix} l & k & l \\ -m_l & q & -m_l \end{pmatrix} \begin{pmatrix} s & \kappa & s \\ -m_s & \pi & -m_s \end{pmatrix} a_l^\dagger (-1)^{l-m_l+s-m_s} a_{l-m_ls-m_s}$$

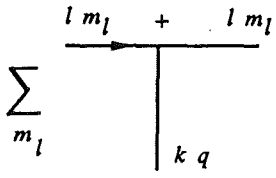
$$= -[\kappa,k]^{\frac{1}{2}} \sum_{m_l,m_s} (-1)^{l-m_l+s-m_s} \begin{pmatrix} l & k & l \\ -m_l & q & m_l \end{pmatrix} \begin{pmatrix} s & \kappa & s \\ -m_s & \pi & m_s \end{pmatrix} a_l^\dagger a_l. \qquad (2.37)$$

Since $s = 1/2$, spin rank κ of the coupled tensor can only be 0 or 1, $\kappa = 0, 1$. The orbital rank k can be from 0 to $2l$, $k = 0, 1, \cdots 2l$. In terms of the angular-diagram this result can be written as



$$a_l^\dagger a_l = -[\kappa,k]^{-\frac{1}{2}} (\mathbf{a}^\dagger \mathbf{a})^{(\kappa,k)}_{\pi,q} = \mathbf{w}^{(\kappa,k)}_{\pi,q}$$

Thus for the spin-independent operators we have



$$a_l^\dagger a_l = -[k]^{-\frac{1}{2}} (\mathbf{a}^\dagger \mathbf{a})^{(0,k)}_{0,q} = \mathbf{w}^{(0,k)}_{0,q} = (2/3)^{\frac{1}{2}} u^{(k)}_q$$

Therefore eq. (2.36) can be written as

$$\sum (a_l^\dagger a_l) \frac{m}{\Delta E} = \sum (nl|r^{k_1}|n'l')(nl|r^{k_2}|n'l')(l||C^{(k_1)}||l')(l'||C^{(k_2)}||l)$$
$$\times \sum_\lambda [\lambda](-1)^{k_1+k_2} \begin{Bmatrix} k_1 & k_2 & \lambda \\ l & l & l' \end{Bmatrix} \begin{pmatrix} k_1 & \lambda & k_2 \\ q_1 & -\gamma & q_2 \end{pmatrix} u^{(\lambda)}_\gamma. \qquad (2.38)$$

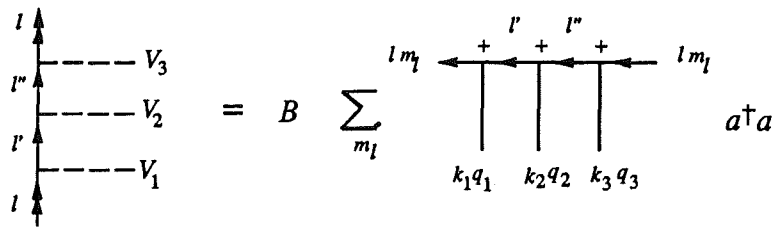
Here the operator $\mathbf{u}^{(\lambda)}_\gamma$ is the effective tensor operator acting only within the one-particle ground configuration nl. Extending this result to an N-particle system (nl^N) an exact same result, namely the eq. (2.32), can be obtained. The many-particle coupling only affects the matrix element of the total one-body effective tensor operator $U^{(\lambda)}_\gamma$ which is defined as

$$U^{(\lambda)}_\gamma \equiv \sum_i^N u^{(\lambda)}_\gamma(i),$$

and the corresponding matrix element between initial and final many-electron states $\langle l^N \alpha SLJM_J | U^{(\lambda)}_\gamma | l^N \alpha'' SL''J''M''_J \rangle$ can be expressed exactly as eq. (2.34).

Thus an equivalent and simplified diagrammatic method of deriving the effective tensor operators for any Goldstone perturbation diagram of the effective Hamiltonian $H_{eff}^{(n)}$ is established.

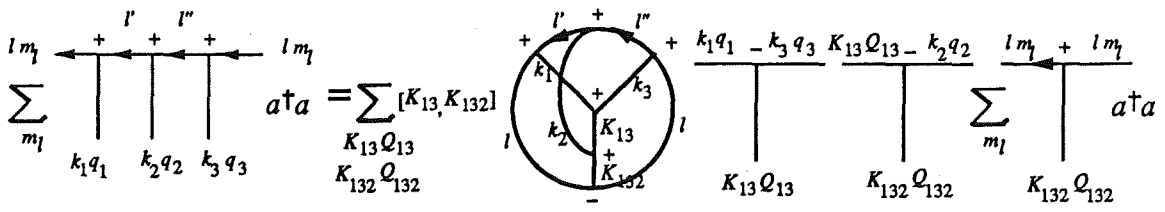
Now we can derive some other Goldstone diagrams in terms of effective tensor operators defined in the last section. For example we choose diagram (b) in Fig. 2.9. Without considering the many-electron coupling diagram (b) represents one electron undergoing three interactions. We do not specify these three interactions (for generality), but suppose that they are all spin-independent, and have the parameterised tensorial form $V_1 = B_{q_1}^{k_1} C_{q_1}^{(k_1)}$, $V_2 = B_{q_2}^{k_2} C_{q_2}^{(k_2)}$, and $V_3 = B_{q_3}^{k_3} C_{q_3}^{(k_3)}$. We have



where the diagram on the right-hand-side denotes the angular diagram part and B represents all other things, the energy denominator, the reduced matrix elements, and the parameters. We suppose that the radial integrals have been absorbed into the parameters, and we write

$$B = \sum_{k_1 q_1 k_2 q_2 k_3 q_3, l' l''} \frac{1}{(\epsilon_l - \epsilon_{l'})(\epsilon_l - \epsilon_{l''})} B_{q_1}^{k_1} B_{q_2}^{k_2} B_{q_3}^{k_3} \langle l||C^{k_1}||l'\rangle\langle l'||C^{k_2}||l''\rangle\langle l''||C^{k_3}||l\rangle. \tag{2.39}$$

Then the angular part can be manipulated by the diagrammatic method in different choice of couplings with equivalent result. One of these choices is the following.

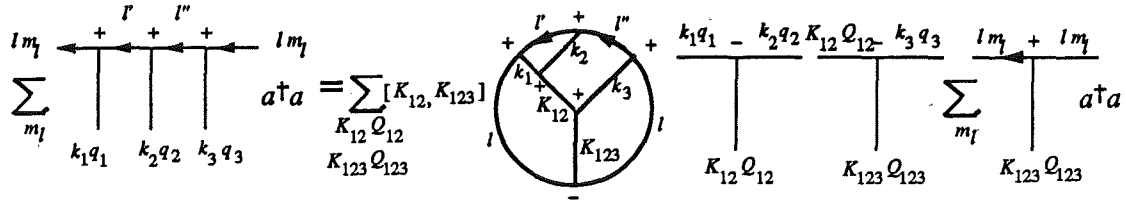


$$= \sum_{K_{13} Q_{13} K_{132} Q_{132}} [K_{13}, K_{132}](-1)^{K_{132}+k_2+k_3+l+l''} \begin{Bmatrix} k_1 & l & l' \\ k_3 & l & l'' \\ K_{13} & K_{132} & k_2 \end{Bmatrix} \times$$

$$\begin{pmatrix} k_1 & K_{13} & k_3 \\ q_1 & -Q_{13} & q_3 \end{pmatrix} \begin{pmatrix} K_{13} & K_{132} & k_2 \\ Q_{13} & -Q_{132} & q_2 \end{pmatrix} \mathrm{w}^{(0,K_{132})}_{0,Q_{132}}. \tag{2.40}$$

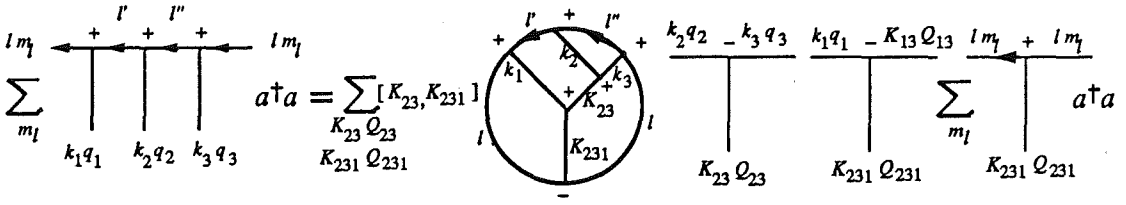
In the above diagrammatic representation on the right-hand-side, the first diagram is a 9j symbol, the next are two 3jm symbols, and the last diagram, associated with the operator $a^\dagger a$ acting within the single electron states lm_l, corresponds to the effective tensor operator $\mathrm{w}^{(0,K_{132})}_{0Q_{132}}$ defined in the last section (immediately above eq. 2.38).

There are also two other different couplings. They are



$$= \sum_{K_{12}Q_{12}K_{123}Q_{123}} [K_{12}, K_{123}](-1)^{K_{123}+l+l'} \begin{Bmatrix} k_1 & k_2 & K_{12} \\ l'' & l & l' \end{Bmatrix} \begin{Bmatrix} K_{12} & k_3 & K_{123} \\ l & l & l'' \end{Bmatrix} \times$$
$$\begin{pmatrix} k_1 & K_{12} & k_2 \\ q_1 & -Q_{12} & q_2 \end{pmatrix} \begin{pmatrix} K_{12} & K_{123} & k_3 \\ Q_{12} & -Q_{123} & q_3 \end{pmatrix} \mathrm{w}^{(0,K_{123})}_{0,Q_{123}}; \tag{2.41}$$

and



$$= \sum_{K_{23}Q_{23}K_{231}Q_{231}} [K_{23}, K_{231}](-1)^{K_{231}+l+l'} \begin{Bmatrix} k_3 & k_2 & K_{23} \\ l' & l & l'' \end{Bmatrix} \begin{Bmatrix} K_{23} & k_1 & K_{231} \\ l & l & l' \end{Bmatrix} \times$$
$$\begin{pmatrix} k_2 & K_{23} & k_3 \\ q_2 & -Q_{23} & q_3 \end{pmatrix} \begin{pmatrix} K_{23} & K_{231} & k_1 \\ Q_{23} & -Q_{231} & q_1 \end{pmatrix} \mathrm{w}^{(0,K_{231})}_{0,Q_{231}}. \tag{2.42}$$

We have $\mathrm{w}^{(0,K_{123})}_{0Q_{123}} = (2/3)^{\frac{1}{2}} u^{(K_{123})}_{Q_{123}}$. When the many-particle coupling is taken into account, only this effective tensor operator $u^{(K_{123})}_{Q_{123}}$ is affected. In that case, we

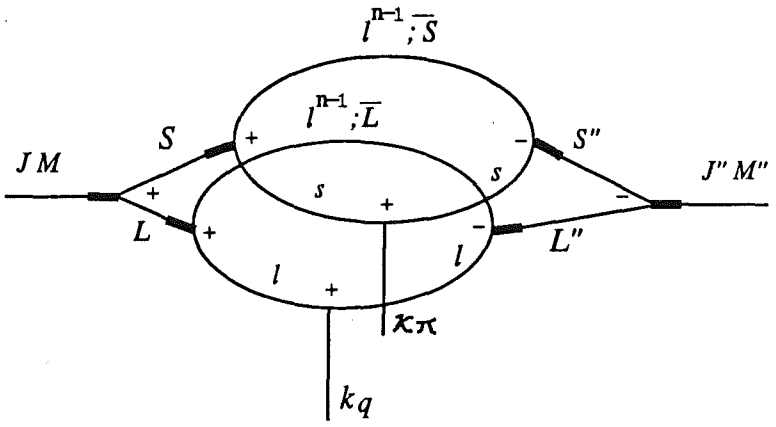
have a full many-particle matrix element

$$\langle l^N \alpha SLJM_J | U^{(K_{123})}_{Q_{123}} | l^N \alpha'' SL''J''M''_J \rangle$$

which is defined by eq. (2.34). The total effective tensor operator $U^{(K_{123})}_{Q_{123}}$ acts only within the initial and the final many-particle states. Then the quantitative calculation can be carried out.

This approach can be applied to any spin-independent one-body Goldstone diagram. When spin-dependent operators, such as the spin-orbit interaction V_{SO} or spin-assisted matter-field interaction H'_S, are involved, a different many-particle matrix element of a general spin-dependent effective tensor operator $\mathbf{W}^{(\kappa,k)t}$ must be defined as

$$\langle l^N \alpha SLJM_J | \mathbf{W}^{(\kappa,k)}_{\pi,q} | l^N \alpha'' SL''J''M''_J \rangle = \sum_{\bar{\Omega}} (l^N \Omega \{ | l^{N-1} \bar{\Omega}, ls)(l^{N-1} \bar{\Omega}'', ls | \} l^N \Omega'') \times$$



Then any spin-dependent Goldstone diagram can be used to derive the effective double tensor operators $\mathbf{w}^{(\kappa,k)}$ for a single particle, and then extend it to the many-particle case by applying the above expression.

CHAPTER 3

Hermiticity, Time Reversal and Tensor Operators

The physical laws of the universe are symmetric under TCP and in the case of the electromagnetic interaction, under each of T, C, and P separately. Each invariance provides selection rules which an operator $\hat{O}$ representing a physical observable has to obey. However an interaction operator may be a contraction of operators $\hat{O}(i)$ acting within subsystems i, such as the matter-field interaction $-e\mathbf{A}\cdot\mathbf{p}/m$; each of these operators, $\mathbf{A}$ or $\mathbf{p}$, need not be time-even (invariant under time reversal) or parity-even (invariant under spatial inversion) (see Stedman 1983). For an electronic operator acting within a given manifold of the fermion states the signature of that physical hermitian operator (or a well defined anti-hermitian operator) under the joint action of hermitian conjugation (H) and time reversal (T) constrains operator's symmetry classification, if its matrix elements are not to vanish within that manifold. This leads to the *time reversal selection rules* (TRSRs) (Abragam and Bleaney (1970), Stedman and Butler (1980), Stedman (1990), Moore and Stedman (1990), Wang and Stedman 1992a,b)). In other words, the symmetry types of the operator in a certain group level can be divided into two classes, HT-even and HT-odd, and such classification is of direct physical interest.

The TRSR has been discussed in these references for one-body operators in the group chain $O_3^J \rightarrow G$, where G is a point group. In section 3.4 and 3.5, see also Wang and Stedman (1992a,b), we will extend such TRSR to a higher group level, the product group level $SU_2^S \times SO_3^L$, and extend to many-body operators. At this product group level, for a one-body operator, the irreps of the SU_2^S group and of the SO_3^L group correspond to the spin rank κ and orbital rank k respectively for an irreducible double tensor operator $\mathbf{W}^{(\kappa,k)}$. Thus, the TRSR within a configuration will restrict the spin-orbital ranks of the HT-even and HT-odd operators distinctively.

Such rule can also be extended to the many-body operators.

Coincidentally, from the 1960s till recently, various hermiticity selection rules have been proposed. These hermiticity rules also intend to restrict the spin and orbital ranks of the irreducible tensor operators, but based on the hermiticity of the operator alone. In section 3.1 I review various "hermiticity rules" and offer for each such rule a counter-example. In section 3.2 I further discuss one of the latest such hermiticity rules in detail and give a counter-example. The properties of the irreducible tensor operator or the coupled tensor operator under the joint action of HT are examined in section 3.3. The TRSRs in the product group level $SU_2^S \times SO_3^L$ for many-body operators, which correct and generalise various "hermiticity rules", are given in section 3.4 and 3.5. In section 3.6 and 3.7 I discuss the relationship of TRSR in a group-subgroup chain and in a product group in general.

3.1 Review of previous "hermiticity rules"

The study of tensor operators and their symmetry transformation properties has a long history. Under the operations of hermitian conjugation (H), time reversal (T), or the joint action HT etc, tensor operators satisfy certain relationships dependent on phase choices. The term, *hermitian tensor operator*, was introduced by Racah (1942). Subsequent authors (Edmonds 1957, Brink and Satchler 1962, Sandars 1969, Wybourne 1970, Judd 1969, Judd 1971, Judd 1977, Judd and Leavitt 1986, Leavitt 1987) use different definitions of a hermitian tensor operator and assert the existence of new selection rules which determine hermiticity from the tensorial rank. After discussing the various definitions we establish a new approach in which tensor operator transformations under the action of hermitian conjugation and time reversal are studied. As a result, we obtain time reversal selection rules (TRSRs) which correct and generalize the selection rules previously assigned to hermiticity.

Eigenfunctions of orbital angular momentum $Y_{lm}(\theta, \phi)$ satisfy the complex conjugation relation $Y_{lm}^*(\theta, \phi) = (-1)^m Y_{l,-m}(\theta, \phi)$ in the most commonly used (CS) phase convention (Condon and Shortley 1935). We may also choose the Edmonds-Fano-Racah (EFR) phase convention with eigenfunctions $D_{lm}(\theta, \phi) \equiv (i)^l Y_{lm}(\theta, \phi)$ and conjugation rule $D_{lm}^*(\theta, \phi) = (-1)^{l+m} D_{l,-m}(\theta, \phi)$ (Edmonds 1957, Fano and Racah 1959).

In quantum mechanics, an operator $\hat{P}$ which represents an observable is required

to be hermitian, i.e. $\hat{P}^\dagger = \hat{P}$; we call such an operator *0-hermitian.* The term *hermitian tensor operator* has a different meaning for different authors. In the following we list five different definitions, which for clarity will be called p-hermitian, for $p = 1$ to 5.

Racah (1942) introduced the tensor operator $T^{(k)}_q$, which has the same symmetry transformation properties as Y_{lm} or D_{lm}; namely under hermitian conjugation, it obeys $T^{(k)\dagger}_q = (-1)^{\epsilon+q} T^{(k)}_{-q}$ where $\epsilon = 0$ in the CS phase and $\epsilon = k$ in the EFR phase. A tensor operator transforming in such a way will be called a *1-hermitian* tensor operator.

A *2-hermitian* tensor operator may be defined by the requirement that its matrix elements, labelled by total angular momentum J and its projection M_J, satisfy

$$\langle JM|T^{(k)}_q|J'M'\rangle = \langle J'M'|T^{(k)}_{-q}|JM\rangle^*. \tag{3.1}$$

According to the Wigner-Eckart theorem this matrix element can be written in terms of the reduced matrix element,

$$\langle JM|T^{(k)}_q|J'M'\rangle = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \langle J||T^{(k)}||J'\rangle. \tag{3.2}$$

A *3-hermitian* tensor operator may then be defined by the requirement that its reduced matrix elements satisfy

$$\langle J||T^{(k)}||J'\rangle = \langle J'||T^{(k)}||J\rangle^*. \tag{3.3}$$

Accordingly, the *2-anti-hermitian* and *3-anti-hermitian* tensor operators will satisfy $\langle JM|T^{(k)}_q|J'M'\rangle = -\langle J'M'|T^{(k)}_{-q}|JM\rangle^*$ and $\langle J||T^{(k)}||J'\rangle = -\langle J'||T^{(k)}||J\rangle^*$ respectively. The former (2-hermitian) is the usage of Judd (1969), and the latter (3-hermitian) is that of Chatterjee and Buckmaster (1990). Chatterjee and Buckmaster go so far as to say that "*there is a unique definition for the hermitian adjoint of a tensor operator and that the Racah definition is not the correct definition.*" Unlike the definition of 1-hermitian operator, these relations are phase-dependent. Racah (1942), also Brink and Satchler (1962) have noted that the matrix element and reduced matrix element of a 1-hermitian tensor operator satisfy the relationships

$$\langle JM|T^{(k)}_q|J'M'\rangle = (-1)^{\epsilon+q}\langle J'M'|T^{(k)}_{-q}|JM\rangle^*; \tag{3.4}$$

$$\langle J||T^{(k)}||J'\rangle = (-1)^{J-J'+\epsilon}\langle J'||T^{(k)}||J\rangle^*. \tag{3.5}$$

The EFR-phased counterpart $(i)^l T^{(k)}_q$ of a CS-phased irreducible tensor operator $T^{(k)}_q$ will be 1-hermitian if $T^{(k)}_q$ is 1-hermitian; however these two operators may not share the same 2-hermitian or 3-hermitian character.

A tensor product is defined by

$$T^{(k_{12})}_{q_{12}} = [T^{(k_1)} T^{(k_2)}]^{(k_{12})}_{q_{12}} \equiv \sum_{q_1,q_2} \begin{pmatrix} k_{12} \\ -q_{12} \end{pmatrix} \begin{pmatrix} k_{12} & k_1 & k_2 \\ -q_{12} & q_1 & q_2 \end{pmatrix} T^{(k_1)}_{q_1} T^{(k_2)}_{q_2}, \tag{3.6}$$

where the first bracket is a 2jm and the second a 3jm symbol (we use the definition of Butler (1981), p45), in this case for SO_3. Here and thereafter a dimension factor $[k_{12}]^{1/2}$ is omitted for the tensor product for simplicity since it will not affect our discussion. The tensor product of n tensors can be written as

$$X^{(K)}_Q = [\cdots [T^{(k_1)} T^{(k_2)}]^{(k_{12})} \cdots T^{(k_n)}]^{(K)}_Q, \tag{3.7}$$

where the square brackets denote the coupling of tensor operators to a new rank. Such a tensor product may correspond to a many-body tensor operator depending on whether the tensors $T^{(k_i)}_{q_i}$ act on different particles.

Using 2-hermitian operators, Judd (1969) said, for such a tensor product $X^{(K)}_Q$, "*A symmetric n-particle*" (we use the term n-body for this) "*scalar operator must be some linear combination of operators of the type* Ξ" ($\Xi \equiv X^{(0)}_0$). "$\cdots$ *Setting* Ξ *between states* ψ *and* ψ' *of* l^n, *and taking the coefficients of fractional parentage to be real, we obtain the result*

$$\langle \psi | \Xi | \psi' \rangle = (-1)^{k_1+k_2+k_3+\cdots+k_n} \langle \psi' | \Xi | \psi \rangle. \tag{3.8}$$

No intermediate ranks like k_{12} *appear in the phase factor. This means that any scalar operator built from single-electron tensors* $T^{k_i}_i$ *is Hermitian if the sum* $k_1 + k_2 + \cdots + k_n$ *is even, and anti-Hermitian if the sum is odd. This result is independent of the particular type of coupling that may be used to produce a scalar resultant.*" Judd (1977, 1986) later described (2-)anti-hermitian operators as not being of physical interest. Wybourne (1969, 1970) extended this usage to higher groups and to spin-dependent operators. He classified one-body operators transforming as $\langle 11 \rangle$ in a symplectic group as "+" (the sum of the spin and orbital ranks being even) and transforming as $\langle 2 \rangle$ as "−". A two-body operator formed from one "+" and one "−" operator was said to be "*non-Hermitian and may be excluded from further consideration.*" Since Wybourne's

definition is a straightforward extension of that of Judd (1969), we use the term 2-hermitian operator for Wybourne's hermitian operator as well. Judd and Wybourne clearly equated 0-hermiticity and 2-hermiticity.

However a counter-example to this equivalence is a 0-hermitian three-body operator $(\mathbf{r}_1 \times \mathbf{p}_2) \cdot \mathbf{r}_3$ where $\mathbf{r}_1$, $\mathbf{p}_2$, and $\mathbf{r}_3$ act on particles 1, 2, and 3 respectively. This operator can be represented by tensor operators as $[[T_1^{(1)}T_2^{(1)}]^{(1)}T_3^{(1)}]^{(0)}$ and is coupled to a scalar with $k_1+k_2+k_3 = 3$. Hence it is 2-anti-hermitian. Note that this operator is time-odd. We will replace this attempted equivalence with a corrected rule, fully incorporating the time reversal character of the operator.

From particle coordinate symmetry considerations alone Wybourne (1970) noted that such an n-body operator $X_Q^{(K)}$, where each one-body operator T_i transforms as the same irrep μ of a group G, will be symmetric (antisymmetric) under the permutation of any pair of particle indices if this n-body operator transforms as the irreps within the symmetric Kronecker product $[\overbrace{\mu \times \mu \times \cdots \times \mu}^{n}]_+ = \mu \otimes \{n\}$ (the antisymmetric product $[\overbrace{\mu \times \mu \times \cdots \times \mu}^{n}]_- = \mu \otimes \{1^n\}$), where $\otimes$ refers to the Littlewood *plethysm*. Judd (1971) introduced the requirement that "*The Kronecker product of two identical representations (corresponding to a bra and a ket) can be separated into a symmetrical and an antisymmetrical part. For non-vanishing matrix elements, the former has to be associated with a hermitian operator, the latter with an anti-hermitian operator.*" We will call this association a definition of a *4-hermitian* operator; and from his use of this association we take Judd (1971) to imply that 4-hermiticity is equivalent to 0-hermiticity. However, a counter-example is the antisymmetric pairwise 4-body operator, $P_1P_2P_3P_4 = -P_4P_2P_3P_1 = P_4P_3P_2P_1$. Since

$$(P_1P_2P_3P_4)^\dagger = P_4^\dagger P_3^\dagger P_2^\dagger P_1^\dagger = P_4P_3P_2P_1 = P_1P_2P_3P_4,$$

this operator is 4-anti-hermitian, yet 0-hermitian. Admittedly such an antisymmetric operator will not give rise to matrix elements in physical applications; however it shows 0-hermiticity and 4-hermiticity are not equivalent. Another counter-example is given below. Hence the symmetrization rule is a stronger rule than 0-hermiticity, and Judd's assertion is incorrect in general.

Judd (1977) and Judd and Leavitt (1986) made this approach more explicit, and wrote such a many-body operator in second quantised form as

$$[[a_1^\dagger a_2^\dagger \cdots a_n^\dagger]^{(\Lambda)}[a_1 a_2 \cdots a_n]^{(\Lambda)}]^{(\Gamma)}, \tag{3.9}$$

where $[a_1^\dagger a_2^\dagger \cdots a_n^\dagger]^{(\Lambda)}$ and $[a_1 a_2 \cdots a_n]^{(\Lambda)}$ transform as the same irrep Λ of the group G, where $1 \cdots n$ denote one-particle-state labels for n particles. Judd (1977) states "*for a Hermitian operator the symmetric part is selected.*" Judd and Leavitt said: "*all operators of physical interest must be Hermitian.* $\cdots$ *The former are Hermitian and correspond to the symmetric part of the product* $\cdots$." Their statement would amount to saying that *the irrep* $\Gamma \in [\Lambda \times \Lambda]_+$ *(the symmetric product) and* $\Gamma \in [\Lambda \times \Lambda]_-$ *(the antisymmetric product) will correspond to (4-)hermitian and (4-)anti-hermitian operators respectively.*

Leavitt (1987), calling these comments of Judd and Leavitt (1986) a "garbled argument", modified this statement to the form: *for an n-body operator with final rank J, if* $n + J$ *is even (odd) the hermitian n-body operators fall into the symmetric product* $\Gamma = [\Lambda \times \Lambda]_+$ *(antisymmetric product* $\Gamma = [\Lambda \times \Lambda]_-$*).* Here a "hermitian" operator can appear in both symmetric and antisymmetric parts, so we shall call this *5-hermiticity.*

A counter-example for the statements of Judd and Leavitt (1986) is the one-body spin-orbital interaction $\mathbf{S} \cdot \mathbf{L}$ which can be expressed as the tensor operator $\mathbf{w}^{(1,1)0}$. At the symplectic group level, the operator $\mathbf{w}^{(1,1)0}$ belongs to the irrep $\langle 11 \rangle$ and is within the antisymmetric part of the product $[\langle 1 \rangle \times \langle 1 \rangle]_-$. According to Judd and Leavitt's statement (1986) this operator is a (4-)anti-hermitian operator. However $\mathbf{S} \cdot \mathbf{L}$ is 0-hermitian. Leavitt's (1987) definition of (5-)hermitian says that if this operator is coupled to a scalar $\mathbf{w}^{(1,1)0}$ in SO_3^J it is (5-)hermitian. This seems to be an improvement for the hermitian rules. However, a counterexample for Leavitt's (5-)hermitian rule can also be found, that is a physical operator such as $\mathbf{S} \times \mathbf{r}$ (or $\mathbf{S} \times \mathbf{L}$). This operator can be expressed as the tensor operator $\mathbf{w}^{(1,1)1}$. Since $\mathbf{w}^{(1,1)1}$ gives $n + J = 2$ and it still belongs to the irrep $\langle 11 \rangle$ which is in the antisymmetric product $[\langle 1 \rangle \times \langle 1 \rangle]_-$, according to Leavitt's (5-)hermiticity, it must be an (5-)anti-hermitian operator (see Judd 1992), yet (0-)hermitian. These particular counter-examples together with the obvious confusion over the definition of "hermitian" tensor operator demand a new approach. Such an approach can be obtained by considering time reversal symmetry combined with hermiticity.

3.2 Further discussions

Along with the discussions of these various definitions of hermitian tensor operators, Judd (1992) gives a more general rule: "$\cdots$ *This is how Leavitt (1987, p3177) derived the formula*

$$[\boldsymbol{a}^\dagger \boldsymbol{a}_Q^{(\kappa,k)K}]^\dagger = (-1)^{\kappa+k+K-Q}\, \boldsymbol{a}^\dagger \boldsymbol{a}_{-Q}^{(\kappa,k)K} \tag{3.10}$$

for the configurations l^N. In the notation of Wang and Stedman it is equivalent to

$$[\boldsymbol{w}_Q^{(\kappa,k)K}]^\dagger = (-1)^{\kappa+k+K-Q}\, \boldsymbol{w}_{-Q}^{(\kappa,k)K} \tag{3.11}$$

The component of $\boldsymbol{w}^{(\kappa,k)}$ for which $Q = 0$ is either hermitian or anti-hermitian according as $\kappa + k + K$ is even or odd. When $Q \neq 0$, it serves to define a daggered operator. $\cdots$ This procedure is easily extended to operators acting on more than one electron at a time. The N-electron operator

$$[\boldsymbol{w}^{(\kappa_1,k_1)K_1}\, \boldsymbol{w}^{(\kappa_2,k_2)K_2} \ldots\, \boldsymbol{w}^{(\kappa_N,k_N)K_N}]_0^{(K)} \tag{3.12}$$

requires a succession of intermediate couplings to define it; however, the ranks associated with these couplings disappear when the hermitian conjugate of (3.12) is formed, with the result that we can conclude that (3.12) is hermitian if

$$\sum_{n=1}^{N}(\kappa_n + k_n) + K \tag{3.13}$$

is even, and anti-hermitian if (3.13) is odd. The expression (3.13) reduces to $\sum k_n$ when $K = 0$ and all $\kappa_n = 0$, in agreement with the special case (Judd 1969, p111) introduced as a potential example of inconsistency by Wang and Stedman." We can take this new statement of the definition of hermitian tensor operator as *6-hermiticity.* This new definition may remove the early inconsistency between Judd's (1969) 2-hermiticity and Leavitt's (1987) 5-hermiticity.

In order to make our argument clear, it is helpful to derive Judd's (1992) result explicitly, and to show that this new rule is still phase-convention-dependent, and so to construct a counterexample. A double tensor operator $\mathbf{w}_{\pi,q}^{(\kappa,k)}$ acts within the spin-orbit space. The symmetry of such a space is denoted by a product group $SU_2^S \times SO_3^L$, where κ and k are the irreps of SU_2^S and SO_3^L respectively. Hence we can equivalently write $\mathbf{w}_{\pi,q}^{(\kappa,k)}$ as

$$\mathbf{w}_{\pi,q}^{(\kappa,k)} \equiv S_\pi^{(\kappa)} T_q^{(k)}, \tag{3.14}$$

where $S_\pi^{(\kappa)}$ and $T_q^{(k)}$ transform within SU_2^S and SO_3^L respectively. Under hermitian conjugation, since the spin and orbital operators commute, we have

$$\mathbf{w}_{\pi,q}^{(\kappa,k)\dagger} = T_q^{(k)\dagger} S_\pi^{(\kappa)\dagger} = (-1)^{\epsilon+\pi+q} S_{-\pi}^{(\kappa)} T_{-q}^{(k)} \tag{3.15}$$

where $\epsilon = 0$ in the CS phase convention and $\epsilon = \kappa + k$ in the EFR phase convention.

We now take coupled bases in SO_3^J, with the coupled tensor operator $\mathbf{w}_Q^{(\kappa,k)K}$ defined by

$$\mathbf{w}_Q^{(\kappa,k)K} \equiv \sum_{\pi,q} \begin{pmatrix} K \\ -Q \end{pmatrix} \begin{pmatrix} K & \kappa & k \\ -Q & \pi & q \end{pmatrix} S_\pi^{(\kappa)} T_q^{(k)}. \tag{3.16}$$

Under hermitian conjugation we have

$$\mathbf{w}_Q^{(\kappa,k)K\dagger} = \sum_{\pi,q} \begin{pmatrix} K \\ -Q \end{pmatrix}^* \begin{pmatrix} K & \kappa & k \\ -Q & \pi & q \end{pmatrix}^* T_q^{(k)\dagger} S_\pi^{(\kappa)\dagger}.$$

Applying the Derome-Sharp Lemma (see Butler (1981)) for the $SO_3 \to SO_2$ case gives

$$\begin{pmatrix} K \\ -Q \end{pmatrix}^* \begin{pmatrix} K & \kappa & k \\ -Q & \pi & q \end{pmatrix}^* = (-1)^{\kappa+k+K} \begin{pmatrix} K \\ Q \end{pmatrix} \begin{pmatrix} K & \kappa & k \\ Q & -\pi & -q \end{pmatrix}.$$

So we have

$$\mathbf{w}_Q^{(\kappa,k)K\dagger} = \sum_{\pi,q} (-1)^{\kappa+k+K} \begin{pmatrix} K \\ Q \end{pmatrix} \begin{pmatrix} K & \kappa & k \\ Q & -\pi & -q \end{pmatrix} (-1)^{\epsilon+\pi+q} T_{-q}^{(k)} S_{-\pi}^{(\kappa)}.$$

Since the spin and the orbital operators commute, we obtain

$$\mathbf{w}_Q^{(\kappa,k)K\dagger} = (-1)^{\kappa+k+K+\epsilon-Q} \mathbf{w}_{-Q}^{(\kappa,k)K}.$$

If we take $Q = 0$ and the CS phase convention, $\epsilon = 0$, we recover eq. (3.11) (eq. (2) of Judd 1992). However it is clear that Judd's (1992) hermitian rule called above 6-hermiticity is *phase-convention-dependent.* If the EFR phase convention is chosen,

$$\mathbf{w}_Q^{(\kappa,k)K\dagger} = (-1)^{K-Q} \mathbf{w}_{-Q}^{(\kappa,k)K},$$

and 6-hermiticity will not guarantee 0-hermiticity.

When this procedure is extended to a many-body operator, we find

$$\left[\mathbf{w}^{(\kappa_1,k_1)K_1} \mathbf{w}^{(\kappa_2,k_2)K_2} \ldots \mathbf{w}^{(\kappa_N,k_N)K_N}\right]_0^{(K)\dagger}$$

$$= (-1)^{\epsilon_n+K+\sum_{n=1}^N (\kappa_n+k_n)} \left[\mathbf{w}^{(\kappa_1,k_1)K_1} \mathbf{w}^{(\kappa_2,k_2)K_2} \ldots \mathbf{w}^{(\kappa_N,k_N)K_N}\right]_0^{(K)}. \tag{3.17}$$

If we choose the CS phase, $\epsilon_n = 0$, we recover eqns. (3.12) and (3.13) (eqns. (3) and (4) of Judd 1992). However, when the EFR phase is chosen, $\epsilon_n = \sum_{n=1}^{N}(\kappa_n + k_n)$, only K is left in eqns. (3.13) and (3.17), and again it illustrates the *phase-convention-dependence* of 6-hermiticity for a many-body operator.

More importantly, even if under a given phase convention (say CS) one has "well" defined (consistent) p-hermitian and p-anti-hermitian tensor operators, such a definition has no necessary connection with the physical requirement of 0-hermiticity. A simple counter-example is the (0-hermitian) physical operators such as $\mathbf{S} \times \mathbf{r}$ or $\mathbf{S} \times \mathbf{L}$ which has the form of a tensor operator $\mathbf{w}^{(1,1)1}$. According to eq. (3.11) (eq. (2) of Judd 1992), since $\mathbf{w}^{(1,1)1}$ gives $\kappa + k + K = 3$, it is 6-anti-hermitian. However it is 0-hermitian.

3.3 Tensor operator symmetries under the joint action HT

A general double tensor operator $\mathbf{w}^{(\kappa,k)}$ under hermitian conjugation (H) will transform (see eq. 3.15) as

$$\mathbf{w}^{(\kappa,k)\dagger}_{\pi,q} = (-1)^{\epsilon+\pi+q}\mathbf{w}^{(\kappa,k)}_{-\pi,-q}$$

where $\epsilon = 0$ in CS phase and $\epsilon = \kappa + k$ in EFR phase. Under time reversal (T) it will transform (see e.g. Abragam and Bleaney 1970) in the manner

$$\overline{\mathbf{w}^{(\kappa,k)}_{\pi,q}} = \tau_o(-1)^{\epsilon+\pi+q}\mathbf{w}^{(\kappa,k)}_{-\pi,-q} \tag{3.18}$$

where the overline denotes the action of time reversal, and the symbol τ_o is the time reversal signature of the operator. A time reversal invariant or time-even operator (such as position $\mathbf{r} \sim \mathbf{w}^{(0,1)}$) has the signature $\tau_o = +1$, and a time-odd operator (such as angular momentum $\mathbf{L} \sim \mathbf{w}^{(0,1)}$) has $\tau_o = -1$. Hence, under the joint action HT the tensor operator $\mathbf{w}^{(\kappa,k)}_{\pi,q}$ obeys

$$\overline{\mathbf{w}^{(\kappa,k)\dagger}_{\pi,q}} = \tau_o\mathbf{w}^{(\kappa,k)}_{\pi,q} \tag{3.19}$$

regardless of the phase convention. The tensor operator $\mathbf{w}^{(\kappa,k)}_{\pi,q}$ goes back to itself with its time reversal signature τ_o under HT. In the following, we shall call an operator with $\tau_o = +1(-1)$ time-even (time-odd) for brevity, strictly it is the HT signature which is meant.

Now let us consider a general tensor product which is appropriate to a general two-body operator in spin-orbit space

$$[\mathbf{w}_1^{(\kappa_1,k_1)}\mathbf{w}_2^{(\kappa_1,k_2)}]^{(\kappa,k)}_{\pi,q} \equiv \sum_{\pi_1,\pi_2,q_1,q_2} \begin{pmatrix} \kappa \\ -\pi \end{pmatrix} \begin{pmatrix} \kappa_1 & \kappa_2 & \kappa \\ \pi_1 & \pi_2 & -\pi \end{pmatrix} \times \begin{pmatrix} k \\ -q \end{pmatrix} \begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{pmatrix} \mathbf{w}^{(\kappa_1,k_1)}_{\pi_1 q_1}\mathbf{w}^{(\kappa_2,k_2)}_{\pi_2 q_2}, \tag{3.20}$$

where $\mathbf{w}^{(\kappa_1,k_1)}_{\pi_1 q_1}$ acts on particle 1 and $\mathbf{w}^{(\kappa_2,k_2)}_{\pi_2 q_2}$ on particle 2. Under the joint action HT we have

$$\begin{aligned} &\overline{[\mathbf{w}_1^{(\kappa_1,k_1)}\mathbf{w}_2^{(\kappa_1,k_2)}]^{(\kappa,k)\dagger}_{\pi,q}} \\ &= \sum_{\pi_1,\pi_2,q_1,q_2} \begin{pmatrix} \kappa \\ -\pi \end{pmatrix} \begin{pmatrix} \kappa_1 & \kappa_2 & \kappa \\ \pi_1 & \pi_2 & -\pi \end{pmatrix} \begin{pmatrix} k \\ -q \end{pmatrix} \begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{pmatrix} \overline{\mathbf{w}^{(\kappa_2,k_2)\dagger}_{\pi_2 q_2}}\ \overline{\mathbf{w}^{(\kappa_1,k_1)\dagger}_{\pi_1 q_1}} \\ &= \tau^1\tau^2[\mathbf{w}_1^{(\kappa_1,k_1)}\mathbf{w}_2^{(\kappa_1,k_2)}]^{(\kappa,k)}_{\pi,q}. \end{aligned} \tag{3.21}$$

Since the 2jm, 3jm, 6j, $\cdots$ are c-numbers, under the joint action HT they are unchanged. We can see that since the spin and orbital operators commute (see eq. 3.15) and the many-body operator must be symmetric under the permutation of any two particle indices (see eq. 3.21), *regardless of the coupling scheme, under the joint action HT the tensor operator and/or the product of such two (or more) tensor operators acting on different particles go back to themselves with the time reversal signature given by the product of those of the component one-body operators.*

In fact, any 0-hermitian operator $\hat{P}$ representing a physical observable may be expanded in terms of any of these p-hermitian tensor operators $\mathbf{w}^{(\kappa,k)}_{\pi,q}$ $(p = 1,\cdots,6)$, i.e.

$$\hat{P} = \sum_{\pi,q} c_{\pi,q}\mathbf{w}^{(\kappa,k)}_{\pi,q}, \qquad \pi = \kappa, \kappa-1, \cdots, -\kappa; \qquad q = k, k-1, \cdots, -k \tag{3.22}$$

regardless of the choice of p or of the choice of phase convention, provided only that the appropriate time reversal signature is chosen, and that the relative phases of the coefficients $c_{\pi,q}$ are suitably adjusted (see Stedman 1990, e.g. problem 3.12 for some examples of the flexibility of this basis choice). It is not possible to use a time-odd tensor operator to expand a time-even physical operator, since no adjustment of phase can alter the time reversal signature of the operator. A time-even (time-odd) physical operator requires a time-even (time-odd) tensor operator for its expansion.

This condition is simply verified by taking the hermitian conjugate and time reversal of eq. (3.22); both H and T are antilinear operators. However the requirement of 0-hermiticity for $\hat{P}$ does not imply that "p-anti-hermitian" tensor operators are physically unimportant. On the contrary, "p-anti-hermitian" tensor operators may be essential for such an expansion.

The true physical restriction will come from the joint action HT, hermitian conjugate and time reversal. Since the physical observable must be hermitian, the key player is the time reversal symmetry of the operator. Under such joint action HT we will obtain *time reversal selection rules* (TRSRs) which correct and generalize the previous "hermiticity" rules.

3.4 Time reversal selection rule

At first, let us take a general form of an n-body operator $P_1P_2\cdots P_n$ acting within the m-electron states $|l^m\rangle$ $(m \geq n)$. By using both second quantisation and group theory language, in the group-subgroup scheme $G_1 \rightarrow G_2$, a matrix element of such an operator can be written as

$$\overline{\langle l^m;\Lambda_1\Lambda_2|}\ [[a^\dagger a]_1^{(\mu)}[a^\dagger a]_2^{(\mu)}\cdots[a^\dagger a]_n^{(\mu)}]^{(\Gamma)}\ |l^m;\Lambda_1\Lambda_2'\rangle. \tag{3.23}$$

where Λ_1, Γ and μ are irreps of the real representation group G_1 for example the symplectic group, and Λ_2, Λ_2' are irreps of G_2. The notation implies that the m-electron states are coupled to definite irrep character; $|l^m;\Lambda_1\Lambda_2\rangle = [a_1^\dagger a_2^\dagger\cdots a_m^\dagger]^{(\Lambda_1\Lambda_2)}|0\rangle$.

Let the n-body operator $P_1P_2\cdots P_n$ transform as the irrep Γ of G_1. Then from Wybourne's symmetrization rule, $\Gamma \in \mu \otimes \{n\}$, while for a nonzero matrix element, $\Gamma \in \Lambda_1 \times \Lambda_1$.

Under the joint action of hermitian conjugation and time reversal, the matrix element (eq. 3.23) satisfies the relationship

$$\begin{aligned}&\overline{\langle l^m;\Lambda_1\Lambda_2|}\ [[a^\dagger a]_1^{(\mu)}[a^\dagger a]_2^{(\mu)}\cdots[a^\dagger a]_n^{(\mu)}]^{(\Gamma)}\ |l^m;\Lambda_1\Lambda_2'\rangle\\ &= \tau_\Lambda^m\tau_o^n\overline{\langle l^m;\Lambda_1\Lambda_2'|}\ [[a^\dagger a]_1^{(\mu)}[a^\dagger a]_2^{(\mu)}\cdots[a^\dagger a]_n^{(\mu)}]^{(\Gamma)}\ |l^m;\Lambda_1\Lambda_2\rangle.\end{aligned} \tag{3.24}$$

where τ_Λ^m is the time reversal signature of the m-electron states, $\overline{\overline{|l^m\rangle}} = \tau_\Lambda^m|l^m\rangle$, where for fermion states $\tau_\Lambda^m = (-1)^m$, and τ_o^n is the time reversal signature of the fermion n-body operator, $\overline{O_n^\dagger} = \tau_o^n O_n$. Following Abragam and Bleaney (1970), Stedman and Butler (1980), Stedman (1990), we obtain a TRSR, that *if* $\tau_\Lambda^m\tau_o^n = +1$ *or* $\tau_\Lambda^m\tau_o^n =$

-1 Γ *can only transform as the symmetric part of the product,* $\Gamma \in [\Lambda_1 \times \Lambda_1]_+$, *or antisymmetric product* $\Gamma \in [\Lambda_1 \times \Lambda_1]_-$ *respectively.*

Hence we obtain the *second rule* of Wang and Stedman (1992a) that within even-electron states, a time-even (time-odd) fermion n-body operator ($n \leq m$) will transform as the symmetric product $\Gamma \in [\Lambda_1 \times \Lambda_1]_+$ (antisymmetric product $\Gamma \in [\Lambda_1 \times \Lambda_1]_-$); and conversely for odd-electron states. This replaces and generalizes the statement of Judd and Leavitt (1986) and also Leavitt (1987). It can be applied to the matrix elements of any operator, whether spin-dependent or spin-independent, scalar or non-scalar, within a manifold.

Now, let us discuss the TRSR for a general one-body spin-orbital tensor operator $\mathbf{w}^{(\kappa,k)}_{\pi,q} \equiv -[\kappa,k]^{-\frac{1}{2}}[\mathbf{a}^\dagger \mathbf{a}]^{(\kappa,k)}$ (see unmarked equation right below eq. (2.37). There is a technical problem to mark it.). Under the joint action HT we have $\overline{\mathbf{w}^{(\kappa,k)\dagger}_{\pi,q}} = \tau_o \mathbf{w}^{(\kappa,k)}_{\pi,q}$ (eq. 3.19). Suppose this one-body operator acts within the one-electron states, its matrix element can be written as

$$\langle\, \overline{lm_l, sm_s}|\ \mathbf{w}^{(\kappa,k)}_{\pi,q}|lm_l', sm_s'\,\rangle.$$

Under the joint action HT, we obtain

$$\langle\, \overline{lm_l, sm_s}|\ \mathbf{w}^{(\kappa,k)}_{\pi,q}|lm_l', sm_s'\,\rangle = \tau_\lambda \tau_o \langle\, \overline{lm_l', sm_s'}|\ \mathbf{w}^{(\kappa,k)}_{\pi,q}|lm_l, sm_s\,\rangle, \tag{3.25}$$

where $\tau_\lambda = -1$ for this one-electron state.

By using the language of group theory, eq. (3.25) is written in the $SU_2^s \times SO_3^l \rightarrow SU_1^{m_s} \times SO_2^{m_l}$ group levels. SU_2^s and SO_3^l denote the spin space and the orbital space respectively. (s,l), and (κ,k) are the irreps of the product group $SO_3^s \times SO_3^l$ for state and the operator respectively. For one-electron states, $s = 1/2$ and l is an integer. Using the *plethysm* (see Wybourne 1970) the symmetric and antisymmetric product can be expressed as $[\lambda \times \lambda]_+ \equiv \lambda \otimes \{2\}$ and $[\lambda \times \lambda]_- \equiv \lambda \otimes \{11\}$ where $\otimes$ denotes the *plethysm.* According to the TRSR (second rule of Wang and Stedman stated above) and applying the general product rule for the product group discussed at section 3.7 (eqns. 3.36 and 3.37) we have

$$\begin{aligned}(\kappa,k)^- \ \in\ (s,l)\otimes\{2\} &= (\tfrac{1}{2}\otimes\{11\}, l\otimes\{11\}) \ +\ (\tfrac{1}{2}\otimes\{2\}, l\otimes\{2\}) \\ &= (0, odd) \ +\ (1, even) \ \rightarrow\ \kappa + k = odd, \qquad (3.26)\\ (\kappa,k)^+ \ \in\ (s,l)\otimes\{11\} &= (\tfrac{1}{2}\otimes\{11\}, l\otimes\{2\}) \ +\ (\tfrac{1}{2}\otimes\{2\}, l\otimes\{11\}) \\ &= (0, even) \ +\ (1, odd) \ \rightarrow\ \kappa + k = even, \qquad (3.27)\end{aligned}$$

where the superscript + (−) denotes that associated operator is time-even, $\tau_o = +1$ (time-odd, $\tau_o = -1$). Equivalently, we can simply condense eqns. (3.26) and (3.27) as $\tau_o = (-1)^{\kappa+k}$. These results are the bases of the first rule of Wang and Stedman (1992a) which will be discussed in the following. Although this result is obtained within one-electron states, it is also valid within many-particle states ($m \geq 1$). A fuller discussion in the whole Racah group chain will be given in chapter 4.

Now considering a general tensor product of spin-orbital n-body tensor operators, we have

$$\overline{[\mathbf{w}_1^{(\kappa_1,k_1)}\mathbf{w}_2^{(\kappa_1,k_2)}\cdots\mathbf{w}_n^{(\kappa_n,k_n)}]}^{(\Xi,K)\dagger}_{\Pi,Q} = \tau_o^n[\mathbf{w}_1^{(\kappa_1,k_1)}\mathbf{w}_2^{(\kappa_1,k_2)}\cdots\mathbf{w}_n^{(\kappa_n,k_n)}]^{(\Xi,K)}_{\Pi,Q} \tag{3.28}$$

where $\tau_o^n = \tau^1\tau^2\cdots\tau^n$ and each τ^i is the time reversal signature of the ith one-body double tensor operator $\mathbf{w}^{(\kappa_i,k_i)}_{\pi_i,q_i}$, κ_i being the spin rank and k_i the orbital rank. We have proved that for a one-body tensor operator $\mathbf{w}^{(\kappa,k)}_{\pi,q}$ its time reversal signature is restricted to be $\tau_o = (-1)^{\kappa+k}$. Hence, for a general n-body tensor product we have

$$\tau_o^n = \tau^1\tau^2\cdots\tau^n = (-1)^{\Omega}; \quad \Omega = \sum_i^n(\kappa_i + k_i). \tag{3.29}$$

We thus obtain the *first rule* of Wang and Stedman (1992a) that *if Ω is even, then $\tau_o^n = +1$; if Ω is odd, then $\tau_o^n = -1$, i.e. a time-even (time-odd) n-body tensor operator must satisfy the requirement that Ω, the sum of the spin and orbit ranks of the individual one-body tensors $\mathbf{w}_i^{(\kappa_i,k_i)}$ is even (odd), if each acts within the same configuration $|l^m\rangle$*. This replaces and generalizes the statements of Judd (1969, 1992), and Wybourne (1970).

We can now find the applications of these selection rules for example to the physical operators $\mathbf{S}\cdot\mathbf{L}$, $\mathbf{S}\times\mathbf{r}$, and $\mathbf{S}\times\mathbf{L}$ used above as the counter-examples. They all have spin-rank 1 and orbit-rank 1 and can be expanded by tensor operator $\mathbf{w}^{(1,1)}$. According to our first rule, the operator $\mathbf{w}^{(1,1)}$ ($\kappa + k = 2$) is allowed to be a *time even* operator to have non-zero matrix element within a configuration. Therefore the time-even operators $\mathbf{S}\cdot\mathbf{L}$ ($\mathbf{w}^{(1,1)0}$) and $\mathbf{S}\times\mathbf{L}$ ($\mathbf{w}^{(1,1)1}$) are allowed to have non-zero matrix element, but the time-odd operator $\mathbf{S}\times\mathbf{r}$ ($\mathbf{w}^{(1,1)1}$) is not.

Moreover, according to our second rule, the time-even operator $\mathbf{w}^{(1,1)}$, which belongs to the irrep $\langle 11\rangle$ of the symplectic group Sp_{4l+2}, can act within the one-electron states ($m = 1$), because its irrep $\langle 11\rangle$ appears in the antisymmetric part of the product $\langle 11\rangle \in [\langle 1\rangle \times \langle 1\rangle]_-$ whether it is scalar ($\mathbf{w}^{(1,1)0}$) or not ($\mathbf{w}^{(1,1)1}$). This time-even one-body operator $\mathbf{w}^{(1,1)}$ can also act within two-electron states ($m = 2$),

because its irrep $\langle 11\rangle$ appears in the symmetric product, $\langle 11\rangle \in [(\langle 11\rangle + \langle 0\rangle) \times (\langle 11\rangle + \langle 0\rangle)]_+$. Operators which do not satisfy these two rules are forbidden to act within the configuration $|l^m\rangle$.

In summary, time reversal considerations have two major consequences. First, they dictate the choice of irreducible tensor operator which is appropriate for the irreducible expansion of a hermitian operator representing a physical observable. Such tensor operators must have the same time reversal signature (even or odd) as the physical operator. This definitive rule replaces all attempts to distinguish the roles of "hermitian" and "anti-hermitian" tensor operators. Second, the irrep Γ appearing in this expansion at the level of some symmetry group G may be restricted by a time reversal selection rule when either the operator as a whole or its one-particle constituents act within states transforming as a certain irrep Λ_1 of G: $\Gamma \in [\Lambda_1 \times \Lambda_1]_\pm$ where the sign $(\pm)$ is given by the product of the time reversal signatures of the relevant operator and of the state.

Our example illustrate two applications of this TRSR. First we examined the TRSR for each single-particle operator within a certain many-particle operator acting within a configuration $|l^m\rangle$, and examined the consequences for the many-particle operator as a whole; $G = SU_2 \times SO_3$, $\Lambda_1 = (S, L)$, $\Gamma = (\kappa, k)$ for spin-orbit space. Second, we required the states to transform as a specified representation of say the symplectic group. Both these strategies may be applied in any situation, and indeed extended to mixed configurations and to cases (e.g. $\Lambda_1 = \langle 11\rangle + \langle 0\rangle$) where the representations are reducible. Such extension means a progressive weakening (loss of constraining power) of the resulting TRSR, offset by a corresponding gain – the enlargement of the domain of applicability of that rule. The one essential requirement for a time reversal selection rule to be obtained is that the time reverse of each bra state should transform like a member of the ket space and vice versa.

3.5 Non-commutative operators, hermiticity, anti-hermiticity, and TRSR.

In the above, the TRSRs were obtained for hermitian (i.e. 0-hermitian) physical operators. If an operator $\hat{P}$ is non-hermitian, the TRSRs are not applicable in this case.

Suppose there are two physical (hermitian) operators $\hat{A}$ and $\hat{B}$ acting on the same

particle. If these two operators commute, $[\hat{A}, \hat{B}] = 0$, the product $\hat{A}\hat{B}$ is hermitian, and the TRSRs apply. If they do not commute, $[\hat{A}, \hat{B}] \neq 0$, $\hat{A}\hat{B}$ is not hermitian, and the TRSRs can not apply. However, such a non-hermitian product of two hermitian operators can be symmetrised and anti-symmetrised as

$$\hat{A}\hat{B} = \frac{1}{2}[\hat{A}\hat{B} + \hat{B}\hat{A}] + \frac{1}{2}[\hat{A}\hat{B} - \hat{B}\hat{A}],$$

where the symmetrised part $\{\hat{A}, \hat{B}\} = \frac{1}{2}[\hat{A}\hat{B} + \hat{B}\hat{A}]$ is hermitian, and has an HT signature of $\tau_+ = \tau^a\tau^b$. The anti-symmetrised part may be called *anti-hermitian* (see e.g. Messiah (1961)), its HT signature being $\tau_- = -\tau_+ = -\tau^a\tau^b$.

Now that both the symmetrised (hermitian) and anti-symmetrised (anti-hermitian) operators have definite HT signatures, TRSRs may be obtained for both of them, but they have opposite selection rules due to the fact that $\tau_- = -\tau_+$. Thus the applications of the TRSRs discussed in the above sections can be extend to the anti-(0-)hermitian operators defined here.

One of the simplest examples is a non-hermitian product operator $\mathbf{rp}$. Since $[\mathrm{r}, \mathrm{p}] \neq 0$ the operator $\mathbf{rp}$ is not hermitian. However, $\mathbf{rp}$ can be written as

$$\mathbf{rp} = \frac{1}{2}(\mathbf{rp} + \mathbf{pr}) + \frac{1}{2}(\mathbf{rp} - \mathbf{pr}) \tag{3.30}$$

The symmetrized part $\hat{C}_+ \equiv \frac{1}{2}(\mathbf{rp} + \mathbf{pr})$ is a hermitian operator and the one-body TRSR can apply. Since $\overline{\hat{C}_+^\dagger} = -\hat{C}_+$ (HT-odd, hermitian and time-odd), the one-body TRSR gives the result that within the same configuration such operator can only have *odd rank* to give a non-zero matrix element. However, the symmetric part $\hat{C}_+$ can only have even rank (the odd rank term vanishes, $\frac{1}{2}(\mathbf{r} \times \mathbf{p} + \mathbf{p} \times \mathbf{r}) = 0$). Therefore the matrix element of $\hat{C}_+$ must be zero. On the other hand, the anti-symmetrised part (anti-hermitian) $\hat{C}_- \equiv \frac{1}{2}(\mathbf{rp} - \mathbf{pr})$ has a HT signature $\tau_- = -\tau_+ = +1$ (HT-even, anti-hermitian and time-odd). The one-body TRSR gives that it *can* have a non-zero matrix element within the configuration if it has *even rank*. In fact, since $\hat{C}_- \equiv \frac{1}{2}[\mathbf{r}, \mathbf{p}] = i\hbar/2$ and so has the (even) rank zero, the conclusion from the TRSR is entirely in agreement with the non-vanishing and c-number nature of this commutator so familiar from Heisenberg's *Uncertainty Principle*.

Therefore, the two rules obtained in section 3.4 (Wang and Stedman 1992a,b) can be further extended to include the *anti-(0)-hermitian* operators defined here. The modification is simply to change the *time-even* to *HT-even*, and *time-odd* to *HT-odd* respectively. HT-even includes time-even hermitian, and time-odd anti-hermitian operators. HT-odd means time-odd hermitian, and time-even anti-hermitian operators.

Under the joint action HT the tensor operators must obey eq. (3.19), and the HT signature is again inherent from the physical operators. This extension, unfortunately, does not serve to reconcile Judd's (1992) variously stated hermitian selection rules.

In general, our TRSRs can be applied to the hermitian and/or anti-hermitian parts of non-hermitian product operators. We shall use this in higher order perturbation theory, which will be discussed in chapters 5 and 6 and will give some novel applications.

3.6 The relationship of TRSR in a group-subgroup chain

When a group chain is used to classify states, a TRSR may be obtained for each group in the chain. This raises several questions. First, do the resulting TRSRs have the same content in each group level? Second, if not, which of the higher group or the subgroup gives novel information? Or does each rule give information not provided by the other? What is the TRSR for a general product group?

Consider for example a group chain, $G_1 \supset G_2$, in which the relevant irreps branch as in Fig. 3.1:

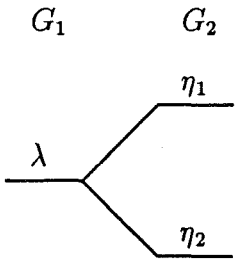


Fig. 3.1

Let λ spans a d-dimensional Hilbert space. The operators acting within these states will transform at the G_1 level as the rep $\mu_1 \in (\lambda \times \lambda) \equiv \lambda^2$. Then in the group G_1 the symmetric and antisymmetric products, $\lambda^2_+ = \lambda \otimes \{2\}$ and $\lambda^2_- = \lambda \otimes \{11\}$, are associated with different HT signatures of the possible irreps of the operator

$$\mu_1^{\pm} \in \lambda \otimes \{2\} \equiv \lambda^2_+, \qquad \mu_1^{\mp} \in \lambda \otimes \{11\} \equiv \lambda^2_-. \tag{3.31}$$

where whether the operator is HT-even (μ_1^+) or HT-odd (μ_1^-) depends on the number of electrons m (see section *3.1*). In case of any confusion we will use the superscripts ($+$ or $-$) to denote HT symmetries of the operator, and the symmetric and antisymmetric product of the rep of the states may be denoted sometimes by the subscripts $+$ and $-$

respectively in this paper. From G_1 to G_2, $\mu_1 \Downarrow \mu_2$, $\mu_1^{\pm} \Downarrow \mu_2^{\pm}$, $\mu_1^{\mp} \Downarrow \mu_2^{\mp}$, $\lambda \Downarrow (\eta_1 + \eta_2)$, $\lambda_+^2 \Downarrow (\eta_1 + \eta_2)_+^2$, and $\lambda_-^2 \Downarrow (\eta_1 + \eta_2)_-^2$. At the subgroup level, in the d^2-dimensional space, we have

$$\mu_2^{\pm} \in (\eta_1 + \eta_2)_+^2 = \eta_1 \otimes \{2\} + \eta_2 \otimes \{2\} + \eta_1 \times \eta_2, \tag{3.32}$$

$$\mu_2^{\mp} \in (\eta_1 + \eta_2)_-^2 = \eta_1 \otimes \{11\} + \eta_2 \otimes \{11\} + \eta_1 \times \eta_2. \tag{3.33}$$

If, at G_2 level, the matrix element represents a coupling within the subspace which is denoted by a single irrep, e.g. η_1, then $\eta_1 \otimes \{2\}$ and $\eta_1 \otimes \{11\}$ will be associated with different HT signature of the operators *within this subspace* η_1, i.e. $\mu_1 \mu_2^{(\pm)} \in \lambda_+^2 (\eta_1)_+^2$ and $\mu_1 \mu_2^{(\mp)} \in \lambda_-^2 (\eta_1)_-^2$. In any group level, if the space (or the subspace) is spanned by a single irrep of that group, TRSR will classify the irreps of the operator, which transforms within this space (or the subspace), into HT-even and HT-odd exclusively.

Since the term $\eta_1 \times \eta_2$ appears in both the symmetric and antisymmetric Kronecker squares of $\eta_1 + \eta_2$, it may be associated with both HT-even and HT-odd operators. However the HT-even $\eta_1 \times \eta_2$ and HT-odd $\eta_1 \times \eta_2$ will have different symmetry *parentage* $\lambda \otimes \{2\}$ and $\lambda \otimes \{11\}$ at G_1 level respectively. This means that if the TRSR in a subgroup may not restrict an irreducible tensor operator as much as in a higher group level a full chain of the irrep labels should be used to classify the operators. The cases $\mu_1 \mu_2 \in \lambda_+^2 (\eta_1 \times \eta_2)$ and $\mu_1 \mu_2 \in \lambda_-^2 (\eta_1 \times \eta_2)$ correspond to two different operators which must have opposite HT signature to couple between η_1 and η_2 only $(\eta_1 \neq \eta_2)$. A practical example will be discussed in section *6.3* for one-body operators in SO_3^J.

In summary, the TRSRs at different levels in a group-subgroup chain have different content, and only by combining all such rules can the full predictive power be realised.

3.7 TRSR in a product group

We now show that if the symmetry group G is a product group $A \times B$, the TRSRs obtained from G and $A \times B$ are mutually consistent. The question of consistency was raised by Prof. B. R. Judd in a private communication.

Considering an operator O^{μ} which transforms as irrep μ of G, we assume the existence of a product basis

$$|\lambda(G)c\rangle = |\alpha(A)a\rangle \, |\beta(B)b\rangle$$

where Greek labels λ, α, and β are the irreps of the group G, A, and B respectively, and Latin labels denote components of these irreps. We denote such a ket transforming as the irrep (α, β) of the product group $A \times B$, for example the spin-orbit wavefunctions in the case $G = SU_2^S \times SO_3^L$. The HT signature τ_λ of $|\lambda c\rangle$ is the product of the corresponding signatures τ_α and τ_β for $|\alpha a\rangle$ and $|\beta b\rangle$, i.e. $\tau_\lambda = \tau_\alpha \tau_\beta$. We also assume that the terms in the operator O^μ are the product of operators O^ρ, O^σ acting within subspaces:

$$O^\mu = O^\rho O^\sigma, \quad (\rho = \rho(A), \quad \sigma = \sigma(B)),$$

i.e. it transforms as the irrep (ρ, σ) of the product group $A \times B$. The HT signature τ_μ of O^μ is the product of those τ_ρ and τ_σ for O^ρ and O^σ, $\tau_\mu = \tau_\rho \tau_\sigma$.

Hence the TRSR in the full group has the form

$$\mu^{\tau_\mu} \in [\lambda \times \lambda]_{\tau_\mu \tau_\lambda}, \quad (\rho, \sigma)^{\tau_\rho \tau_\sigma} \in [(\alpha, \beta) \times (\alpha, \beta)]_{\tau_\rho \tau_\sigma \tau_\alpha \tau_\beta}. \tag{3.34}$$

In the subspaces, the TRSRs have the form

$$\rho^{\tau_\rho} \in [\alpha \times \alpha]_{\tau_\rho \tau_\alpha}, \quad \sigma^{\tau_\sigma} \in [\beta \times \beta]_{\tau_\sigma \tau_\beta}. \tag{3.35}$$

Since each $\tau_i = \pm 1$ $(i = \mu, \rho, \sigma, \lambda, \alpha, \beta)$, $[\lambda \times \lambda]_+ \equiv \lambda \otimes \{2\}$, $[\lambda \times \lambda]_- \equiv \lambda \otimes \{11\}$, $\lambda = (\alpha, \beta)$, we have

$$\lambda \otimes \{2\} = (\alpha, \beta) \otimes \{2\} = (\alpha \otimes \{11\}, \beta \otimes \{11\}) + (\alpha \otimes \{2\}, \beta \otimes \{2\}), \tag{3.36}$$

$$\lambda \otimes \{11\} = (\alpha, \beta) \otimes \{11\} = (\alpha \otimes \{11\}, \beta \otimes \{2\}) + (\alpha \otimes \{2\}, \beta \otimes \{11\}). \tag{3.37}$$

We see from an inspection of these equations that the relations which link the various symmetric and/or antisymmetric products between G and $A \times B$ and the TRSRs obtained from G and $A \times B$ are consistent.

If the product group $A \times B$ is a subgroup of G and one irrep λ of G branches to more than one irrep of $A \times B$, $\lambda \Downarrow (\alpha_1, \beta_1) + (\alpha_2, \beta_2) + \cdots$, the relationship of the TRSRs obtained from G and $A \times B$ is basically the same as discussed in section 3.6.

CHAPTER 4

Orthogonal Many-body Operators, Time Reversal Selection Rules, and Associated Symmetry Classification

In chapter 3 we have extended the TRSRs to the product group $SU_2^S \times SO_3^L$ level, and the correction and generalisation have been made for previous "hermiticity rules". In this chapter we discuss here the TRSRs which may apply to the matrix elements for a more general group–subgroup scheme, i.e. all possible group levels in a Racah group chain (Racah 1949) suitable for many-electron states LS-coupling scheme. The motivation is, firstly, that in a higher group level we may gain more novel information different from the lower level and such HT-even and HT-odd classification for many-body operators is of directly physical interest. Secondly, as mentioned in chapter 1, there is a traditional problem to identify the symmetry type of many-body operators at symplectic group level, such as the Coulomb interaction and the Trees operators, and therefore HT-even and HT-odd classification according to TRSRs is very helpful.

The unitary symmetry of a general orthogonal n-body operator is discussed in section 4.1. In section 4.2 the choice of the basis is discussed and the branching rules, $U_{14} \rightarrow Sp_{14}$, of fermion n-body operators are given. We show that TRSRs may be obtained at the level of the symplectic group (section 4.2.2) but not usefully at the unitary group level (section 4.2.1). These n-body operators are then classified into HT-even and HT-odd operators at the Sp_{14} level (section 4.3), and the results are compared with the classifications of Judd and Leavitt (1986) and Leavitt (1987).

For the case of one-body operators, more details are given in section 4.4, in which the TRSRs are obtained at $SU_2^S \times SO_3^L$ level (section 4.4.1). Additional complications at the SO_3^J level are discussed in section 4.4.2.

The branching rules in the chain $U_{14} \rightarrow Sp_{14} \rightarrow SU_2^S \times [SO_7 \rightarrow SO_3^L]$ for HT-even spin-independent two-body operators are given in sections 4.5. The branching rules in the same group chain for HT-even spin-dependent and HT-odd two-body operators are also listed in tables given in section 4.7. To obtain these branching rules I am greatly benefited from the computer program *SCHUR* which is developed by Professor Brian Wybourne and his students. I have also obtained his kindly direct help. These branching rules together with time reversal symmetry considerations have great value in practical applications, generalizing and modifying known results for two-body operators such as the correlation crystal field (Newman 1971) in section 4.5.1. The various classifications of two-body operators are investigated, with repercussions for the theory of the Coulomb interaction within a shell and for atomic and nuclear spectroscopy (section 4.6). Similar applications can also be found for n-body operators with $n \geq 3$.

4.1 Unitarity of orthogonal n-body operators

Judd *et al.* (1982) noted that operators whose coefficients parameterized spectral fitting should be orthogonalized. In the language of group theory (Judd 1984): if the operators $O_1^{\mu_1}$ and $O_2^{\mu_2}$ transform as the irreps μ_1 and μ_2 of group G respectively, these two operators are orthogonal if $\mu_1 \times \mu_2 \not\supset 0$, i.e. if the product of μ_1 and μ_2 does not contain the identity irrep. This requires that μ_1 differs from μ_2^*. Extending such a rule throughout a group chain, two operators must have at least one irrep label different for some group in that chain if they are to be orthogonal. Unfortunately in practice the orthogonality condition is not always satisfied by operators such as Slater's Coulomb operators, Trees operators, and Racah Coulomb operators which will be discussed in section 4.6.

We may classify the eigenstates of the zero-order Hamiltonian $\hat{H}^{(0)}$ within the atomic (or nuclear) configuration l^m by the irreducible representation (irrep) $\{\lambda\}$ of the unitary group U_{4l+2}, with $|l^m\rangle$ transforming as $\{1^m\}$ and $\hat{H}^{(0)}$ as the identity irrep $\{0\}$. A one-body interaction operator transforming as the irrep $\{\mu_1\}$ of U_{4l+2} will be written as

$$O_1^{\{\mu_1\}} = [a^{\dagger\{1\}} a^{\{1\}^*}]^{\{\mu_1\}}, \tag{4.1}$$

where the asterisk denotes complex conjugate, and $\{\mu_1\} \in \{1\} \times \{1\}^* = \{1;1\} + \{0\}$ where $\{1;1\}$ is a composite irrep (Black *et al.* 1983). Applying the orthogonality

restriction the unitary scalar part ($\{0\}$) of the one-body operator can not be an independent orthogonal operator, since it is indistinguishable from $\hat{H}^{(0)}$. So orthogonal $O_1^{\{\mu_1\}}$ can only transform as the irrep $\{1;1\}$ of U_d, i.e. $\{\mu_1\} = \{1;1\}$.

The two-body interaction operators, orthogonal to the one-body operators, can similarly be written as

$$O_2^{\{\mu_2\}} = [[a^\dagger a]_1^{\{1;1\}}[a^\dagger a]_2^{\{1;1\}}]^{\{\mu_2\}} \tag{4.2}$$

where $\{\mu_2\} \in \{1;1\} \times \{1;1\}$. The permutation symmetric operator can only transform as the symmetric Kronecker product (as for Wybourne 1970)

$$\{\mu_2\} \in \{1;1\} \otimes \{2\} = \{11;11\} + \{2;2\} + \{1;1\} + \{0\}, \tag{4.3}$$

where $\otimes$ denotes the *plethysm*. Since a two-fermion (two-boson) ket state $|l^2\rangle$ transforms as the irrep $\{11\}$ ($\{2\}$) and the bra $\langle l^2|$ transforms as $\{11\}^*$ ($\{2\}^*$) of U_d, where for the l-shell electrons $d = 4l+2$ and for IBM bosons in nuclear physics $d = \sum_j (2l_j+1)$ (e.g. Arima and Iachello (1978)), the interaction operators are restricted to transform as

$$\{\mu_2\}_f \in \{11\}^* \times \{11\} = \{11;11\} + \{1;1\} + \{0\}, \tag{4.4}$$

$$\{\mu_2\}_b \in \{2\}^* \times \{2\} = \{2;2\} + \{1;1\} + \{0\}. \tag{4.5}$$

Since O_2 must be orthogonalized to both the one-body operator O_1 transforming as $\{1;1\}$ and $\hat{H}^{(0)}$ transforming as $\{0\}$, *such a fermion (boson) two-body operator can only transform as the irrep* $\{11;11\}$ *(*$\{2;2\}$*) of* U_d. This conclusion is also in conformity with the result that the two-body operator must have a null matrix element within the one-particle states.

In general *an orthogonalized fermion (boson) n-body interaction operator will transform as the unique irrep* $\{1^n;1^n\}$ *(*$\{n;n\}$*) of the unitary group* U_d.

4.2 Choice of group chain

We classify the m-particle eigenstates $|l^m;\Psi\rangle$ of the unperturbed Hamiltonian and irreducible tensor operator O_n representing an n-body physical interaction, by the irrep labels λ_i and μ_i of each group G_i, respectively, in a chain; $G_1 \rightarrow G_2 \rightarrow \cdots$ where each G_i corresponds to a symmetry group of the unperturbed Hamiltonian.

Table 4.1 Branching rules of f-shell n-body operators, $U_{14} \rightarrow Sp_{14}$

U_{14}	Sp_{14}
$\{0\}$	$\langle 0\rangle$
$\{1;1\}$	$\langle 2\rangle, \langle 1^2\rangle$
$\{11;11\}$	$\langle 2^2\rangle, \langle 21^2\rangle, \langle 1^4\rangle, 2\langle 1^2\rangle, \langle 0\rangle$
$\{1^3;1^3\}$	$\langle 2^3\rangle, \langle 2^21^2\rangle, \langle 21^4\rangle, 2\langle 21^2\rangle, \langle 2\rangle, \langle 1^6\rangle, 2\langle 1^4\rangle, \langle 1^2\rangle$
$\{1^4;1^4\}$	$\langle 2^4\rangle, \langle 2^31^2\rangle, \langle 2^21^4\rangle, 2\langle 2^21^2\rangle, \langle 21^6\rangle, 2\langle 21^4\rangle, \langle 2^2\rangle, \langle 21^2\rangle, 2\langle 1^6\rangle, 3\langle 1^4\rangle, 2\langle 1^2\rangle, \langle 0\rangle$
$\{1^5;1^5\}$	$\langle 2^5\rangle, \langle 2^41^2\rangle, \langle 2^31^4\rangle, 2\langle 2^31^2\rangle, \langle 2^3\rangle, 2\langle 2^21^4\rangle, \langle 2^21^2\rangle, \langle 21^6\rangle, 3\langle 21^4\rangle, 2\langle 21^2\rangle, \langle 2\rangle,$ $2\langle 1^6\rangle, 2\langle 1^4\rangle, \langle 1^2\rangle$
$\{1^6;1^6\}$	$\langle 2^6\rangle, \langle 2^51^2\rangle, 2\langle 2^41^2\rangle, \langle 2^4\rangle, \langle 2^31^4\rangle, \langle 2^31^2\rangle, 2\langle 2^21^4\rangle, 2\langle 2^21^2\rangle, \langle 2^2\rangle, \langle 21^6\rangle, \langle 21^4\rangle,$ $\langle 21^2\rangle, 2\langle 1^6\rangle, 2\langle 1^4\rangle, 2\langle 1^2\rangle, \langle 0\rangle$
$\{1^7;1^7\}$	$\langle 2^7\rangle, \langle 2^51^2\rangle, \langle 2^5\rangle, \langle 2^31^4\rangle, \langle 2^31^2\rangle, \langle 2^3\rangle, \langle 21^6\rangle, \langle 21^4\rangle, \langle 21^2\rangle, \langle 2\rangle$

In the case of n fermions in an atomic or nuclear shell with orbital angular momentum l, the popular group chain (Racah 1949)

$$U_{4l+2} \rightarrow Sp_{4l+2} \rightarrow SU_2^S \times [SO_{2l+1} \rightarrow SO_3^L]$$

will be used in this paper. Further branching rules in this group chain for the N-electron states, which is commonly used to classify and label these states, were listed by Nielson and Koster (1963). This chain is only suitable for the LS-coupling scheme. For jj-coupling a different group chain was chosen (see Wybourne 1970).

The branching rules of n-body operators in the f-shell from U_{14} to Sp_{14} are given in Table 4.1. A general matrix element $\langle l^m;\Psi|O_n|l^m;\Psi'\rangle$ can be written in the full LS-coupling (Racah) group chain as

$$\langle l^m;\{\lambda_1\}\langle\lambda_2\rangle\ {}^{2S+1}[\lambda_3],SLJM\ |O_n^{\{\mu_1\}\langle\mu_2\rangle(\kappa,[[\mu_3]k])KQ}\ |l^m;\{\lambda_1\}\langle\lambda_2\rangle\ {}^{2S'+1}[\lambda_3'],S'L'J'M'\rangle \tag{4.6}$$

where $\{\lambda_1\}$ and $\{\mu_1\}$ are the irreps of U_{4l+2}, $\langle\lambda_2\rangle$ and $\langle\mu_2\rangle$ of Sp_{4l+2}, and $[\lambda_3]$ and $[\mu_3]$ of SO_{2l+1}, etc. Under the joint action of hermitian conjugate (H) and time reversal (T) this matrix element then obeys (Wang and Stedman 1992a),

$$\overline{\langle l^m;\Psi|O_n^{\mu_i}|l^m;\Psi'\rangle} = \tau_\lambda\tau_o\overline{\langle l^m;\Psi'|O_n^{\mu_i}|l^m;\Psi\rangle}. \tag{4.7}$$

The same relation holds for the reduced matrix elements since the 2jm and 3jm symbols are c-numbers and symmetric under the joint action HT,

$$\overline{\langle l^m;\lambda_i\lambda_{i-1}||O_n^{\mu_i\mu_{i-1}}||l^m;\lambda_i\lambda_{i-1}'\rangle} = \tau_\lambda\tau_o\overline{\langle l^m;\lambda_i\lambda_{i-1}'||O_n^{\mu_i\mu_{i-1}}||l^m;\lambda_i\lambda_{i-1}\rangle}. \tag{4.8}$$

We can then obtain the second rule of Wang and Stedman (1992a) of TRSR at each group level in the chain: *within states with an even number m of electrons, a HT-even (HT-odd) fermion n-body operator with $n \leq m$ will transform within the symmetric product $\mu_i^+ \in [\lambda_i \times \lambda_i]_+$ (antisymmetric product $\mu_i^- \in [\lambda_i \times \lambda_i]_-$); and conversely for an odd number m of electrons.* Equivalently we can abbreviate the above statements to $\mu_i^{\tau_o} \in [\lambda_i \times \lambda_i]_{\tau_o \tau_\lambda}$.

4.2.1 TRSR in the unitary group U_{4l+2}

At the unitary group level, the reduced matrix element can be written as

$$\langle \{1^m\}\langle\lambda_2\rangle || \, O_n^{\{\mu_1\}\langle\mu_2\rangle} || \{1^m\}\langle\lambda_2'\rangle \rangle. \tag{4.9}$$

Since the m-particle ket state transforms as $\{1^m\}$ and the bra transforms contragrediently as $\{1^m\}^*$ at U_{4l+2} level, this requires $\{\mu_1\}$ to be in the Kronecker product of two inequivalent irreps $\{1^m\}$ and $\{1^m\}^*$; this Kronecker product cannot be symmetrized. Therefore the unitary irrep labels of the operator $\{\mu_1\}$, such as $\{1;1\}$, are not restricted by HT symmetry.

4.2.2 TRSR in the symplectic group Sp_{4l+2}

At the Sp_{4l+2} level, the reduced matrix element

$$\langle \langle\lambda_2\rangle \, {}^{2S+1}[\lambda_3] || \, O^{\langle\mu_2\rangle[\mu_3]} || \langle\lambda_2\rangle \, {}^{2S'+1}[\lambda_3'] \rangle. \tag{4.10}$$

involves only real irreps so that the relevant Kronecker product can be symmetrized or antisymmetrized. Hence the TRSR can be derived and within a given manifold the irreps of the symplectic group Sp_{4l+2} can be associated with HT-even or HT-odd n-body operators. The TRSR can also be extended within a extended manifold which may be represented by a reducible representation $\langle\lambda_{re}\rangle$ (rep) of Sp_{4l+2}. Details of the TRSR are given in the next section.

4.3 Orthogonal n-body operators and their HT symmetries

Judd and Leavitt (1986) decomposed n-body operators in the d-shell in their Table 4.2. Leavitt (1987) gave the branching rules for the f-shell in his Table 4.4 but a few errors are noted below. While Judd and Leavitt classify the operators as hermitian or antihermitian within their phase convention, chapter 3 and Wang and Stedman (1992a,b)

show that the physically important classification is given by the combined symmetry of the hermiticity and time reversal. We now follow through the consequences of this re-analysis for a full classification of such operators.

The symmetry transformation properties of an n-body operator are independent of the m-particle states within which such operator acts, and such matrix element $\langle l^m;\Psi|O_n|l^m;\Psi'\rangle$ can be rewritten as an n-body operator acting within n-particle states with appropriate cfp's. In other words, the TRSRs obtained within l^n can also be applied in l^m $(m > n)$, and we may choose $m = n$ without loss of generality.

An n-fermion state transforms as the irrep $\{1^n\}$ of U_{4l+2}, which branches to the rep $\langle\lambda_{re}\rangle = \langle 1^n\rangle + \cdots$ of Sp_{4l+2}, and the symmetrized (antisymmetrized) Kronecker square corresponds to $\{1^n\}\otimes\{2\}$ ($\{1^n\}\otimes\{11\}$ respectively). On the other hand, at the unitary group level, since

$$\{1^n\}^*\times\{1^n\} = \{1^n;1^n\} + \{1^{n-1};1^{n-1}\} + \cdots + \{0\}, \tag{4.11}$$

we obtain

$$\{1^n;1^n\} = \{1^n\}^*\times\{1^n\} - \{1^{n-1}\}^*\times\{1^{n-1}\} \tag{4.12}$$

where $\{1^n;1^n\}$ is the irrep appropriate to a fermion n-body operator in U_{4l+2}. In Sp_{4l+2} this operator transforms as a rep $\langle\mu_{re}\rangle_n$, the reduction of $\{1^n;1^n\}$. So we can write

$$\{1^n;1^n\} = (\{1^n\}^*\times\{1^n\} - \{1^{n-1}\}^*\times\{1^{n-1}\})\Downarrow\langle\mu_{re}\rangle_n \tag{4.13}$$

Since the reps $\{1^n\}^*\times\{1^n\}$, $\{1^n\}^*\times\{1^n\}^*$, and $\{1^n\}\times\{1^n\}$ give the same reduction to Sp_{4l+2} then we obtain

$$(\{1^n\}\times\{1^n\} - \{1^{n-1}\}\times\{1^{n-1}\})\Downarrow\langle\mu_{re}\rangle_n, \tag{4.14}$$

where the first term corresponds to a Kronecker square of the rep of the n-particle state, and the second term of the $(n-1)$-particle state. We can now apply the second rule of Wang and Stedman (1992a): if n is even, then the HT-even (HT-odd) n-body operator transforms as $\langle\mu_{re}\rangle_n^+$ ($\langle\mu_{re}\rangle_n^-$ respectively) in Sp_{4l+2} and we have

$$(\{1^n\}\otimes\{2\} - \{1^{n-1}\}\otimes\{11\})\Downarrow\langle\mu_{re}\rangle_n^+, \tag{4.15}$$

$$(\{1^n\}\otimes\{11\} - \{1^{n-1}\}\otimes\{2\})\Downarrow\langle\mu_{re}\rangle_n^- \tag{4.16}$$

and conversely for n odd.

Table 4.2 HT-even and HT-odd fermion n-body operators (n-ops) in the f-shell, $U_{14} \rightarrow Sp_{14}$

N-ops	HT-even	HT-odd
$\{0\}$	$\langle 0\rangle$	
$\{1;1\}$	$\langle 1^2\rangle$	$\langle 2\rangle$
$\{11;11\}$	$\langle 2^2\rangle, \langle 1^4\rangle, \langle 1^2\rangle, \langle 0\rangle$	$\langle 21^2\rangle, \langle 1^2\rangle$
$\{1^3;1^3\}$	$\langle 2^21^2\rangle, \langle 21^2\rangle, \langle 1^6\rangle, \langle 1^4\rangle, \langle 1^2\rangle$	$\langle 2^3\rangle, \langle 21^4\rangle, \langle 21^2\rangle, \langle 2\rangle, \langle 1^4\rangle$
$\{1^4;1^4\}$	$\langle 2^4\rangle, \langle 2^21^4\rangle, \langle 2^21^2\rangle, \langle 21^4\rangle, \langle 2^2\rangle, \langle 1^6\rangle, 2\langle 1^4\rangle,$ $\langle 1^2\rangle, \langle 0\rangle$	$\langle 2^31^2\rangle, \langle 2^21^2\rangle, \langle 21^6\rangle, \langle 21^4\rangle, \langle 21^2\rangle, \langle 1^6\rangle, \langle 1^4\rangle,$ $\langle 1^2\rangle$
$\{1^5;1^5\}$	$\langle 2^41^2\rangle, \langle 2^31^2\rangle, \langle 2^21^4\rangle, \langle 2^21^2\rangle, \langle 21^6\rangle, \langle 21^4\rangle,$ $\langle 21^2\rangle, \langle 1^6\rangle, \langle 1^4\rangle, \langle 1^2\rangle$	$\langle 2^5\rangle, \langle 2^31^4\rangle, \langle 2^31^2\rangle, \langle 2^3\rangle, \langle 2^21^4\rangle, 2\langle 21^4\rangle, \langle 21^2\rangle,$ $\langle 2\rangle, \langle 1^6\rangle, \langle 1^4\rangle$
$\{1^6;1^6\}$	$\langle 2^6\rangle, \langle 2^41^2\rangle, \langle 2^4\rangle, \langle 2^31^4\rangle, \langle 2^21^4\rangle, \langle 2^21^2\rangle,$ $\langle 2^2\rangle, \langle 21^4\rangle, \langle 1^6\rangle, \langle 1^4\rangle, \langle 1^2\rangle, \langle 0\rangle$	$\langle 2^51^2\rangle, \langle 2^41^2\rangle, \langle 2^31^2\rangle, \langle 2^21^4\rangle, \langle 2^21^2\rangle, \langle 21^6\rangle,$ $\langle 21^2\rangle, \langle 1^6\rangle, \langle 1^4\rangle, \langle 1^2\rangle$
$\{1^7;1^7\}$	$\langle 2^51^2\rangle, \langle 2^31^2\rangle, \langle 21^6\rangle, \langle 21^2\rangle$	$\langle 2^7\rangle, \langle 2^5\rangle, \langle 2^31^4\rangle, \langle 2^3\rangle, \langle 21^4\rangle, \langle 2\rangle$

To illustrate the content of these two equations, we choose the fermion 4-body operator as an example. HT-even ($\langle\mu_{re}\rangle_4^+$) and HT-odd ($\langle\mu_{re}\rangle_4^-$) 4-body operators will be

$$\{1^4\}\otimes\{2\}-\{1^3\}\otimes\{11\}=(\{2^4\}+\{2^21^4\}+\{1^8\}-\{2^21^2\}-\{1^6\})\Downarrow\langle\mu_{re}\rangle_4^+, \quad (4.17)$$

$$\{1^4\}\otimes\{11\}-\{1^3\}\otimes\{2\}=(\{2^31^2\}+\{21^6\}-\{2^3\}-\{21^4\})\Downarrow\langle\mu_{re}\rangle_4^- \quad (4.18)$$

respectively. For the case of the f-shell, branching from U_{14} down to Sp_{14} gives

$$\langle\mu_{re}\rangle_4^+=\langle 2^4\rangle+\langle 2^21^4\rangle+\langle 2^21^2\rangle+\langle 2^2\rangle+\langle 21^4\rangle+\langle 1^6\rangle+2\langle 1^4\rangle+\langle 1^2\rangle+\langle 0\rangle, \quad (4.19)$$

$$\langle\mu_{re}\rangle_4^-=\langle 2^31^2\rangle+\langle 2^21^2\rangle+\langle 21^6\rangle+\langle 21^4\rangle+\langle 21^2\rangle+\langle 1^6\rangle+\langle 1^4\rangle+\langle 1^2\rangle. \quad (4.20)$$

Leavitt's result $\langle 2^41^2\rangle$ for a 4-body operator should be replaced by $\langle 2^31^2\rangle$. Likewise his result $\langle 0\rangle$ for a 5-body operator should be replaced by $\langle 1^2\rangle$.

Applying eqns. (4.15) and (4.16) for even-body operators and conversely for odd-body operators we can classify n-body operators within the f-shell in Sp_{14} into HT-even and HT-odd operators (see Table 4.2). These results are general, whether these operators act within any particle states ($m > n$), are spin-dependent or spin-independent, scalar or non-scalar.

4.4 TRSR of the one-body operators

According to Table 4.1 a one-body interaction operator will transform as the irrep $\{1;1\}$ of U_{4l+2}, and as the rep $\langle 2\rangle + \langle 11\rangle$ of Sp_{4l+2}. From Table 4.2, we have obtained that HT-even (HT-odd) fermion one-body operators acting within the same configuration must transform as the irrep $\langle 11\rangle$ ($\langle 2\rangle$) of Sp_{4l+2}.

Within the group chain $U_{4l+2} \rightarrow Sp_{4l+2} \rightarrow SU_2^S \times [SO_{2l+1} \rightarrow SO_3^L]$, one-body operators may then be classified in Table 4.3 (following Wybourne 1970 and with the extension of time reversal classification). One-body operators transforming as $\langle 2\rangle$ (or $\langle 11\rangle$) in Sp_d can be written in $SU_2^S \times SO_3^L$ as double tensor operators $\mathbf{w}^{(\kappa,k)}$ with $\kappa + k$ odd (even, respectively). We conclude that *one-body operators* $w^{(\kappa,k)}$ *acting within the same configuration are HT-even (HT-odd), if* $\kappa + k$ *is even (odd respectively).* Accordingly, the electric dipole interaction $\mathbf{E}\cdot\mathbf{r}$ (which is HT-even and has tensorial form $\mathbf{w}^{(0,1)}$) is forbidden within any configuration. This is in agreement with the Laporte parity rule, but it is logically distinct from it, and holds when parity is not a valid symmetry as in the theory of parity non-conservation in atomic physics by the weak interaction (Sandars 1977).

Table **4.3** The symmetry classification of one-body tensor operators

U_{4l+2}	Sp_{4l+2}	$SU_2^S \times [SO_{2l+1}$	$SO_3^L]$	$\mathbf{w}^{(\kappa,k)}$ in $SO_3^S \times SO_3^L$	TRSRs
$\{1;1\}$	$\langle 2\rangle$	$^3[200]$	$2,4,6,\cdots 2l$	$\mathbf{w}^{(1,2)}, \mathbf{w}^{(1,4)}, \cdots \mathbf{w}^{(1,2l)}$	
		$^3[000]$	0	$\mathbf{w}^{(1,0)}$	HT-odd
		$^1[110]$	$1,3,5,\cdots 2l-1$	$\mathbf{w}^{(0,1)}, \mathbf{w}^{(0,3)}, \cdots \mathbf{w}^{(0,2l-1)}$	
	$\langle 11\rangle$	$^3[110]$	$1,3,5,\cdots 2l-1$	$\mathbf{w}^{(1,1)}, \mathbf{w}^{(1,3)}, \cdots \mathbf{w}^{(1,2l-1)}$	HT-even
		$^1[200]$	$2,4,6,\cdots 2l$	$\mathbf{w}^{(0,2)}, \mathbf{w}^{(0,4)}, \cdots \mathbf{w}^{(0,2l)}$	

4.4.1 TRSR in $SU_2^S \times SO_3^L$ group

The discussion at this group level has been given in section 3.4. Here we shall not repeat it. Basically, at this group level we discuss a matrix element under the joint action HT:

$$\langle\, \overline{lm_l, sm_s}||\, \mathbf{w}^{(\kappa,k)}_{pi,q}||lm_l', sm_s'\,\rangle = -\tau_o\langle\, \overline{lm_l', sm_s'}||\, \mathbf{w}^{(\kappa,k)}_{\pi,q}||lm_l, sm_s\,\rangle. \qquad (4.21)$$

By applying the TRSR (Abragam and Bleaney 1970, Stedman and Butler 1980, and also being re-sated in section 3.4) we obtain the results of eqns. (3.26) and (3.27) given in section 3.4. These results can be condensed as $\tau_o = (-1)^{\kappa+k}$, i.e. the sum of the spin-orbital ranks of an HT-even (HT-odd) one-body operator $\mathbf{w}^{(\kappa,k)}$ must be *even* (*odd* respectively). A generalisation for the n-body operators results in the first rule (eq. 3.29) given by Wang and Stedman (1992a).

4.4.2 TRSR in SO_3^J group

In SO_3^J the states and the one-body operators are denoted by ${}^{2S+1}L_J$ and $\mathbf{w}^{(\kappa,k)K}$ respectively, where the operator $\mathbf{w}^{(\kappa,k)K}$ takes a fully coupled form. Since even a one-electron state will span more than one irrep of SO_3^J, the complexity (discussed in section 3.6 in a general form) is expected.

First, we choose a one f-electron state as an example (without loss of generality). In SO_3^J there are only two different J-states, ${}^2F_{7/2}$ and ${}^2F_{5/2}$. Applying the TRSR to the matrix element $\langle\, \overline{(7/2+5/2),M}||\, \mathbf{w}^{(\kappa,k)K}_{Q}||(7/2+5/2),M'\,\rangle$ in SO_3^J, and using the eqns. (3.32) and (3.33) we have

$$\begin{aligned} K^- \;\in\; & (\tfrac{7}{2}+\tfrac{5}{2})\otimes\{2\} = (\tfrac{7}{2})\otimes\{2\} + (\tfrac{5}{2})\otimes\{2\} + (\tfrac{7}{2})(\tfrac{5}{2}) \\ & = (1+3+5+7)+(1+3+5)+(1+2+3+4+5+6), \qquad (4.22) \\ K^+ \;\in\; & (\tfrac{7}{2}+\tfrac{5}{2})\otimes\{11\} = (\tfrac{7}{2})\otimes\{11\} + (\tfrac{5}{2})\otimes\{11\} + (\tfrac{7}{2})(\tfrac{5}{2}) \\ & = (0+2+4+6)+(0+2+4)+(1+2+3+4+5+6). \qquad (4.23) \end{aligned}$$

According to the discussion of section 3.6, we can obtain the following general conclusions: (i) If the one-body operator $\mathbf{w}^{(\kappa,k)K}$ acts within the same J-values which may correspond to two different $|LS\rangle$, the final rank K *is restricted* to be even (odd) for HT-even (HT-odd) operators only. (ii) If $\mathbf{w}^{(\kappa,k)K}$ acts between two different J-values, the final rank K *is unrestricted.* In the case (ii) we are not able to distinguish the HT symmetry of the operators by their SO_3^J symmetry. However the different HT symmetries of the operators do have different symmetry *parentage* (see below).

Second, according to section 4.4.1 we have $\tau_o = (-1)^{\kappa+k}$, i.e. the HT symmetries of the one-body operators $\mathbf{w}^{(\kappa,k)K}$ are strictly restricted by their$SU_2^S \times SO_3^L$ symmetry. By using the branching rules from $SU_2^S \times SO_3^L \rightarrow SO_3^J$ we obtain Table 4.4.

From this Table 4.4 we can see that the final ranks K from 1 to 6 appear in both HT-even and HT-odd operators (in agreement with the above two equations)

Table 4.4 Fermion one-body operators $\mathbf{w}^{(\kappa,k)K}$ in SO_3^J

HT-odd:	$\mathbf{w}^{(1,0)1}$,	$\mathbf{w}^{(0,1)1}$,	$\mathbf{w}^{(0,3)3}$,	$\mathbf{w}^{(0,5)5}$,
	$\mathbf{w}^{(1,2)1,2,3}$,	$\mathbf{w}^{(1,4)3,4,5}$,	$\mathbf{w}^{(1,6)5,6,7}$,	
HT-even:		$\mathbf{w}^{(0,2)2}$,	$\mathbf{w}^{(0,4)4}$,	$\mathbf{w}^{(0,6)6}$,
	$\mathbf{w}^{(1,1)0,1,2}$,	$\mathbf{w}^{(1,3)2,3,4}$,	$\mathbf{w}^{(1,5)4,5,6}$,	

but with different $SU_2^S \times SO_3^L$ *parentage*. Eqns. (4.22) and (4.23), rather than Table 4.4, specify the subspaces within which these operators can act. As in section 3.6, only by combining TRSRs from all levels can the full predictive power of TRSR be obtained.

4.5 TRSRs of fully classified two-body operators

A fermion two-body interaction operator, which transforms as the irrep $\{11;11\}$ of U_{4l+2}, will transform as the rep $\langle 2^2\rangle + \langle 2^2 1^2\rangle + \langle 1^4\rangle + 2\langle 1^2\rangle + \langle 0\rangle$ of the symplectic group Sp_{4l+2}. According to table 4.2 of section 3, all HT-even (HT-odd) two-body operators will span the rep $\langle 2^2\rangle + \langle 1^4\rangle + \langle 1^2\rangle + \langle 0\rangle$ ($\langle 2^2 1^2\rangle + \langle 1^2\rangle$ respectively). Since these two-body operators span a bigger space than do the one-body operators, the relationships of the TRSRs in the group-subgroup scheme become more complicated, but the principle is still that discussed in section 3.6.

Now in the f-shell we branch these irreps of the operators according to the group chain $U_{14} \supset Sp_{14} \supset SU_2^S \times [SO_7 \supset G_2 \supset SO_3^L]$. Grouped as HT-even, HT-odd, spin-singlet (spin-independent), spin-triplet, and spin-quintet, they are listed in Tables 4.5, 4.7 to 4.11.

4.5.1 Spin-independent two-body operators $s(e)_i^{(0,K)}$, their one-body components, and Newman's rule for correlation crystal field

Since a HT-odd two-body interaction is not relevant to most problems in atomic and nuclear physics, we discuss only the HT-even two-body interactions, and for simplicity spin-independent interactions such as the Coulomb interaction, the orbit-orbit interaction, and the correlation crystal field. These all correspond to $s(e)_i^{(0,K)}$ ($i = 1, 2, \cdots, 14$) operators in Table 4.5. These 14 operators correspond to 14 irreps

Table 4.5 Spin-independent HT-even fermion two-body operators $s(e)_i^{(0,K)}$

U_{14}	Sp_{14}	$SU_2 \times [SO(7)$	G(2)	SO(3)]	$s(e)_i^{(0,K)}$ *	$g_i^{(K)}$	o_i
{11;11}	⟨22⟩	^{1}[400]	(40)	$0, 2, 3, 4^2, 5, 6^2,$			
				$7, 8^2, 9, 10, 12$	$s(e)_1^{(0,K)}$: ⟨22⟩^{1}[400](40)K	$g_{10}^{(K)}$	o_7
		^{1}[220]	(22)	$0, 2, 4, 5, 6, 8, 10$	$s(e)_2^{(0,K)}$: ⟨22⟩^{1}[220](22)K	$g_9^{(K)}$	o_6
			(21)	$2, 3, 4, 5, 7, 8$	$s(e)_3^{(0,K)}$: ⟨22⟩^{1}[220](21)K	$g_7^{(K)}$	
			(20)	$2, 4, 6$	$s(e)_4^{(0,K)}$: ⟨22⟩^{1}[220](20)K	$g_5^{(K)}$	
		^{1}[111]	(20)	$2, 4, 6$	$s(e)_5^{(0,K)}$: ⟨22⟩^{1}[111](20)K	$g_{11}^{(K)}$	
			(10)	3	$s(e)_6^{(0,3)}$: ⟨22⟩^{1}[111](10)3	$g_{11}^{(3)}$	
			(00)	0	$s(e)_7^{(0,0)}$: ⟨22⟩^{1}[111](00)0	$g_{11}^{(0)}$	o_5
		^{1}[200]	(20)	$2, 4, 6$	$s(e)_8^{(0,K)}$: ⟨22⟩^{1}[200](20)K	$g_3^{(K)}$	
		^{1}[000]	(00)	0	$s(e)_9^{(0,0)}$: ⟨22⟩^{1}[000](00)0	–	o_4
	⟨1^4⟩	^{1}[220]	(22)	$0, 2, 4, 5, 6, 8, 10$	$s(e)_{10}^{(0,K)}$: ⟨1^4⟩^{1}[220](22)K	$g_8^{(K)}$	o_3
			(21)	$2, 3, 4, 5, 7, 8$	$s(e)_{11}^{(0,K)}$: ⟨1^4⟩^{1}[220](21)K	$g_6^{(K)}$	
			(20)	$2, 4, 6$	$s(e)_{12}^{(0,K)}$: ⟨1^4⟩^{1}[220](20)K	$g_4^{(K)}$	
	⟨11⟩	^{1}[200]	(20)	$2, 4, 6$	$s(e)_{13}^{(0,K)}$: ⟨11⟩^{1}[200](20)K	$g_2^{(K)}$	
	⟨0⟩	^{1}[000]	(00)	0	$s(e)_{14}^{(0,0)}$: ⟨0⟩ ^{1}[000](00)0	–	o_2

* The notations following each $s(e)_i^{(0,K)}$ operator denote a set of the irreps of $Sp_{14} \supset SU_2 \times [SO_7 \supset G_2 \supset SO_3]$

of G_2 and each of them has at least one different irrep labels in the group chain $U_{14} \supset \cdots \supset SU_2 \times G_2$. Therefore they are orthogonal to and independent of each other. The ranks (Ξ, K) of these operators are the irreps of $SU_2^S \times SO_3^L$, and here for spin-singlet are $(0, K)$. As previously explained, we classify these operators by their time reversal signature rather than their signature under hermitian conjugation given by Judd (1977). The entries in the second last column labelled by $g_i^{(K)}$ are the corresponding notations of Judd (1977). The last column gives SO_3 scalar o_i operators which will be discussed in section 4.6.

In Table 4.5, there are many irrep labels of SO_3^L which correspond to the K values of $s(e)_i^{(0,K)}$. On the other hand, these spin-independent two-body operators can also be constructed in the form of a tensor product $V_{12}^{(k_1 k_2)K} \equiv [V_1^{(k_1)} V_2^{(k_2)}]^{(K)}$ in SO_3^L, where $V_i^{(k_i)}$ is a one-body spin-independent operator acting on particle i. We have $K \in k_1 \times k_2$ where k_1, k_2, and K are the irreps of SO_3^L. We can construct all possible HT-even two-body operators $V_{12}^{(k_1 k_2)K}$ and compare with the results of table 4.5 to see if these two independent ways match. For the HT-even operator $V_{12}^{(k_1 k_2)K}$

Table **4.6** Spin-singlet HT-even fermion two-body operators $V_{12}^{(k_1k_2)K} = [T^{(k_1)}T^{(k_2)}]^{(K)}$

(k_1k_2)	K	(k_1k_2)	K
(11)	0, 2	(13)	2, 3, 4
(33)	0, 2, 4, 6	(15)	4, 5, 6
(55)	0, 2, 4, 6, 8, 10	(35)	2, 3, 4, 5, 6, 7, 8
(22)	0, 2, 4	(24)	2, 3, 4, 5, 6
(44)	0, 2, 4, 6, 8	(26)	4, 5, 6, 7, 8
(66)	0, 2, 4, 6, 8, 10, 12	(46)	2, 3, 4, 5, 6, 7, 8, 9, 10

$k_1 + k_2$ must be *even* (see eq. 3.29 and Wang and Stedman 1992a). At the SO_3 level, if $k_1 = k_2 = k$ then only the symmetric part of the product $[k \times k]_+ \ni K$ is symmetric under permutation of coordinates (Wybourne 1970). Since k is an integer, in SO_3 such a symmetric product can only produce even K. Hence the case K odd and $k_1 = k_2$, such as $V_{12}^{(11)1}$, is forbidden.

Let us consider the case of the correlation crystal field (CCF) of Newman (1971) and Newman and Ng (1989), in which CCF operators have the structure of $V_{12}^{(k_1k_2)K} \equiv [V_1^{(k_1)}V_2^{(k_2)}]^{(K)}$. The above rules were also derived by Newman (1971) using time reversal and hermiticity explicitly together with the interchange phase of the 3jm symbol. The above argument is equivalent to this in its conclusion but is not dependent on explicit manipulation of the 3jm symbols within a phase convention.

For the case of $k_1 \neq k_2$ the coupled rank K is not necessarily even. However if the states are restricted to the same J-manifold for example, then K has to be even (odd) for a HT-even (HT-odd) operator by applying the TRSR in this J-manifold (see section 4.4.2). In addition Newman (1971) pointed out that for a special point group symmetry ($C_{\infty v}$) by applying the superposition model and on the assumption that the parity of a tensor operator $V_q^{(k)}$ is $(-1)^k$ then K is always even. This may be seen more directly by saying that Newman's parity assumption is the consequence of the joint parity being $(-1)^{k_1+k_2} = +1$ (i.e. $k_1 + k_2$ is even) and the fact that only even-ranked even-parity operators j^+ of O_3 branch to an invariant of $C_{\infty v}$. The above TRSR for many-body operators has generalized Newman's conclusion in a more elegant way using group theory, and can be applied not only to CCF but also to any spin-independent two-body operator such as the Coulomb or the orbit-orbit interaction.

All of the possible HT-even two-body $V_{12}^{(k_1k_2)K}$ operators satisfying the above

TRSR for the f-shell are listed in table 4.6. The number of occurrences of any possible irrep K of SO_3 in these two tables, Tables 4.5 and 4.6, is exactly the same. This checks the consistency of regarding the operator transforming as the irrep $\{11;11\}$ of U_{4l+2} as the two-body operator constructed from the tensor product $[\mathbf{w}^{(\kappa_1,k_1)}\mathbf{w}^{(\kappa_2,k_2)}]^{(\Xi,K)}$, with operators such as $[\mathbf{w}^{(0,0)}\mathbf{w}^{(\kappa,k)}]^{(\kappa,k)}$ and $[\mathbf{w}^{(0,0)}\mathbf{w}^{(0,0)}]^{(0,0)}$ being excluded from orthogonal consideration. The last two operators, in fact, have the symmetry of a one-body operator or of the unperturbed Hamiltonian $\hat{H}^{(0)}$ operator;

$$[\mathbf{w}^{(0,0)}\mathbf{w}^{(\kappa,k)}]^{(\kappa,k)} = \mathbf{w}^{(\kappa,k)} \rightarrow \{1;1\},$$

$$[\mathbf{w}^{(0,0)}\mathbf{w}^{(0,0)}]^{(0,0)} = \mathbf{w}^{(0,0)} \rightarrow \{0\}.$$

4.5.2 One-body TRSR in uncoupled bases for a pure two-body operator

A general pure (first-order) two-body operator can be written in tensorial form as

$$\hat{O}_{12} = \sum_{i\neq j}^{N} \hat{O}_i\hat{O}_j = \sum_{i\neq j,\kappa,k\cdots} C(\kappa,k,\kappa',k')[\mathbf{w}_i^{(\kappa,k)}\mathbf{w}_j^{(\kappa',k')}]^{(\Xi,K)}, \tag{4.24}$$

where $\hat{O}_i$ is a one-body operator acting on particle i. In the minimal domain, the two-particle states $|l^2\rangle$, the matrix element of such an operator can be written in coupled form as

$$\langle l^2|\hat{O}_{12}|l^2\rangle = \sum_{\kappa,k,\kappa',k'} C\langle l^2|\,[\mathbf{w}_1^{(\kappa,k)}\mathbf{w}_2^{(\kappa',k')}]^{(\Xi,K)}|l^2\rangle. \tag{4.25}$$

The second rule of Wang and Stedman (1992a) (see eq. 3.24) is obtained by using coupled bases, and gives restriction on the ranks (Ξ, K) of the operator. Also, according to the first rule (see eq 3.29) the sum of the spin-orbital ranks of the component operators, $\kappa + k + \kappa' + k'$, are restricted to be even (odd) for HT-even (HT-odd) operators.

In addition, in uncoupled bases we also have

$$\langle l^2|\mathbf{w}_1^{(\kappa,k)}\mathbf{w}_2^{(\kappa',k')}|l^2\rangle = A\langle l|\mathbf{w}_1^{(\kappa,k)}|l\rangle\ \langle l|\mathbf{w}_2^{(\kappa',k')}|l\rangle. \tag{4.26}$$

Thus each one-body component has to obey the TRSR for the one-body operators $\mathbf{w}^{(\kappa,k)}$ (section 4.4.1), i.e. within a configuration the TRSR allows $\mathbf{w}^{(\kappa,k)}$ to be HT-even (HT-odd) if its rank $\kappa+k$ is even (odd). The overall HT symmetry of the n-body operator is the product of that of all its one-body components, and the consequence of this is just eq. (3.29), the first rule of Wang and Stedman (1992a).

We conclude that the overall HT-even two-body spin-independent operators in Table 4.6 have two kinds of structure, $[V_i^{(+)}V_j^{(+)}]^{(K)}$ and $[V_i^{(-)}V_j^{(-)}]^{(K')}$; the former (latter) has the property that its one-body components can only represent HT-even (HT-odd) physical one-body operators. The operators in Table 4.5 are each a linear combination of the operators in Table 4.6.

4.6 Orthogonal scalar two-body operators and atomic spectra

In addition to the interest of the TRSRs discussed in chapter 3 and previous sections in this chapter, we are also interested in applying the HT classifications of many-body operators associated with their symmetry classification to physical applications such as energy level structure, transition processes. Here we discuss one of such applications, the atomic energy level structure due to the Coulomb interaction (V_C) and the Trees operators (V_T) between electrons in the light of TRSR.

For the purpose of obtaining the energy level splitting in atomic physics the first order approximation to the system Hamiltonian $\hat{H}^{(1)}$ is taken as the Coulomb interaction (V_C) between the electrons within a dominant configuration (Slater 1929, Condon and Shortley 1935, Racah 1949). Latter on the second-order Coulomb interaction and the orbit-orbit interactions, known as Trees terms (V_T), are also considered (Trees 1951, Rajnak and Wybourne 1963, Morrison and Rajnak 1971). More discussion about the Trees terms will be given in section 5.5. Judd and Crosswhite (1984) discussed the operators V_C and V_T plus the three-body operators in the light of orthogonality.

The Coulomb interaction $\hat{H}_C = \sum_{i\neq j} e^2/r_{ij}$ is a time-even two-body operator, and is a scalar operator in SO_3. Within a configuration Slater's theory (Slater 1929) parameterized the Coulomb interaction with Slater parameters F_k. There are various forms to express this Coulomb interaction in terms of parameterised tensorial form (see Judd 1963), either with different definition of the tensor operators or with different parameters. We may choose the following expression (see Judd (1963), eq. 8-17)

$$\hat{H}_C = \sum_{i\neq j,k} f_k [V_i^{(k)} V_j^{(k)}]^{(0)}, \tag{4.27}$$

where $f_k = c_k F_k$, e.g. $f_2 = 84F_2$ etc. The rank k can only be even, corresponding to time-even one-body component operators $V_i^{(+)}$, $V_j^{(+)}$ if its matrix elements are not to

vanish within a configuration. Trees (1951) first noted that by adding similar scalar two-body tensor operators but with *odd* rank k the accuracy of the energy level fitting is greatly improved. Thus the first-order correction to the independent particle and central field approximation (see chapters 1 and 2) can be taken as $H^{(1)} = V_C + V_T$. Writing in tensorial form in the f-shell, we have

$$\begin{aligned}\hat{H}^{(1)} &= \sum_{i\neq j}\{f_0[V_i^{(0)}V_j^{(0)}]^{(0)} + f_2[V_i^{(2)}V_j^{(2)}]^{(0)} + f_4[V_i^{(4)}V_j^{(4)}]^{(0)} + f_6[V_i^{(6)}V_j^{(6)}]^{(0)} \\ &\quad +\alpha[V_i^{(1)}V_j^{(1)}]^{(0)} + \beta[V_i^{(3)}V_j^{(3)}]^{(0)} + \gamma[V_i^{(5)}V_j^{(5)}]^{(0)}\}. \qquad (4.28)\end{aligned}$$

Here the last three operators correspond to the Trees operators. All these tensor operators only have well defined symmetry properties at the SO_3 group level, and they all transform as a SO_3 scalar. Thus they are not orthogonal to each other (Judd 1984) and lead to the problem that when adding V_T into $H^{(1)}$ the parameters for V_C must change accordingly. This problem is called "one of the most disconcerting features" in parameterised energy level fittings.

Since Racah group chain successively describes the many-electron states, the fact that the operators in eq. (4.28) do not separately have well defined symmetry properties in higher group level is apparently a disadvantage. Racah (1949) constructed another four Coulomb operators e_0, e_1, e_2, and e_3, which are the linear combinations of four Slater operators (for the f-shell). They have well defined symmetry properties, i.e. transform as a definite irrep of a group, in the group chain $SO_7 \supset G_2 \supset SO_3$ as

$$\begin{aligned} e_0&: \ [000](00)0, \qquad & e_1&: \ [000](00)0, \\ e_2&: \ [400](40)0, \qquad & e_3&: \ [220](22)0. \end{aligned}$$

Likewise three Trees operators can also be reconstructed to form more symmetrised operators (see Wybourne 1970) as

$$e'_\alpha: \ [000](00)0, \qquad e'_\beta: \ [111](00)0, \qquad e'_\gamma: \ [220](22)0.$$

Thus $H^{(1)}$ can also be re-written in a more symmetric form in the group chain $SO_7 \supset G_2 \supset SO_3$ as

$$\hat{H}^{(1)} = E^0e_0 + E^1e_1 + E^2e_2 + E^3e_3 + \alpha'e'_\alpha + \beta'e'_\beta + \gamma'e'_\gamma \qquad (4.29)$$

where the parameters E^i are linear combinations of the Slater parameters F_i.

If one examines the orthogonality properties (see section 4.1) of these operators e_i and e'_i the orthogonality condition (Judd *et al.* 1982, Judd and Crosswhite 1984,

Uylings 1984), i.e. each operator transforms as a set irreps in a group chain different from any others, is still not fully satisfied. Some of the operators e_i and e'_i transform as the same irreps in the chain $SO_7 \supset G_2 \supset SO_3$. The problem of varying parameters still exists (see Judd and Crosswhite 1984). Nevertheless Racah's construction of more symmetric operators e_i and e'_i is a step, if not a final one, towards orthogonal operators.

In addition, these operators e_i and e'_i do not have well defined symplectic symmetry because these lower symmetry irreps may come from different irreps at Sp_{14} level. This is related with non-orthogonal problem. In order to have well defined symmetry properties for many-body operators at the $U_{4l+2} \supset Sp_{4l+2}$ group levels we can go another way around, looking for some physical classification at the $U_{4l+2} \supset Sp_{4l+2}$ group levels. As mentioned before, Judd (1982,1984) proposed orthogonality consideration which leads to the result that an orthogonal n-body operator transform uniquely as an irrep $\{1^n;1^n\}$ of the unitary group U_{4l+2}. Judd and Leavitt (1986) and Leavitt (1987) tried to classify the symplectic symmetries according to the hermiticity consideration which has been corrected by Wang and Stedman (1992a,b) and also by section 4.3 from the consideration of time reversal symmetry. We have also further reduced the HT-even spin-independent two-body operators along the full Racah chain $U_{14} \supset Sp_{14} \supset SU_2 \times [SO_7 \supset G_2 \supset SO_3]$ for the f-shell in Table 4.5. Apparently V_C and V_T operators belong to this table and they are scalar in SO_3. We list SO_3 scalar operators in Table 4.5 at below,

$$
\begin{aligned}
s(e)_1^{(0,0)}\text{:}\quad & \{11;11\}\langle 22\rangle^1[400](40)0, && \rightarrow\ o_7\\
s(e)_2^{(0,0)}\text{:}\quad & \{11;11\}\langle 22\rangle^1[220](22)0, && \rightarrow\ o_6\\
s(e)_7^{(0,0)}\text{:}\quad & \{11;11\}\langle 22\rangle^1[111](00)0, && \rightarrow\ o_5\\
s(e)_9^{(0,0)}\text{:}\quad & \{11;11\}\langle 22\rangle^1[000](00)0, && \rightarrow\ o_4\\
s(e)_{10}^{(0,0)}\text{:}\quad & \{11;11\}\langle 1^4\rangle^1[220](22)0, && \rightarrow\ o_3\\
s(e)_{14}^{(0,0)}\text{:}\quad & \{11;11\}\langle 0\rangle\ ^1[000](00)0, && \rightarrow\ o_2\\
& \{0\}\langle 0\rangle\ ^1[000](00)0, && \rightarrow\ o_1.
\end{aligned}
$$

where the notation o_i is due to Judd and Crosswhite (1984). The last, case o_1, is excluded from being an orthogonal two-body operator since it is indistinguishable from the system's unperturbed Hamiltonian $\hat{H}^{(0)}$, it shifts the centre of gravity of the spectrum. We can see that each operator o_i is orthogonal to each other since it has at least one irrep label different. We can propose this orthogonal set as a basis for

discussing energy splitting due to Coulomb and Trees operators:

$$H^{(1)} = D_1 o_1 + D_2 o_2 + D_3 o_3 + D_4 o_4 + D_5 o_5 + D_6 o_6 + D_7 o_7. \tag{4.30}$$

Each operator o_i is a linear combination of $[V_i^{(k)} V_j^{(k)}]^{(0)}$ with $k = 0, 1, 2, \cdots, 6$. This is a natural generalization of Racah's approach to the operators e_i. Judd and Crosswhite (1984) have obtained the same set of operators o_i and identified them in terms of the operators e_i and e_i' as the following,

$$\begin{aligned} o_1 &\rightarrow e_0, & o_5 &\rightarrow e'_\beta, \\ o_2 &\rightarrow -, & o_6 &\rightarrow \Omega, \\ o_3 &\rightarrow e_3 + \Omega, & o_7 &\rightarrow e_2, \\ o_4 &\rightarrow -, \end{aligned}$$

where o_2 and o_4 are unidentified, and Ω will be explained below. They then mentioned: "$\cdots$ the o_i (operators) are not satisfactory for the purposes of theoretical spectroscopy. For example, e_3 no longer appears as a separate operator, but instead in the combination $o_3 - o_6$." Thus they formed further linear combinations to form another set of operators.

However, first, there is an error in their identification, namely $o_3 \rightarrow e_3 + \Omega$. According to Judd (1963),

$$\Omega = 11[V_i^{(1)} V_j^{(1)}]_0^{(0)} - 3[V_i^{(5)} V_j^{(5)}]_0^{(0)}. \tag{4.31}$$

At the symplectic group level $V_i^{(1)}$ and $V_i^{(5)}$ belong to the irrep $\langle 2 \rangle$ (see table 4.3). The symmetric product of $\langle 2 \rangle$ does not contain $\langle 1111 \rangle$ (see eq. 4.33). Thus Ω can not transform like o_3, and o_3 should be identified as e_3 only. We will prove in the following that the o_3 and o_7 operators are the linear combinations of the Coulomb operators $[V_i^{(k)} V_j^{(k)}]^{(0)}$ with k even only. In fact, $o_3 = e_3$ and $o_7 = e_2$. The operator o_5 is the linear combination of the Trees' operators $[V_i^{(k)} V_j^{(k)}]^{(0)}$ with k odd only, and $o_5 = e'_\beta$. The operators o_2, o_4, and o_6 could be linear combinations of both Coulomb and Trees operators. Second, although some of the operators o_i do not arise from a single physical origin, these o_i operators ($i = 1, 2, \cdots, 7$) are still preferable with some important advantages mentioned at the beginning of this section, namely their orthogonality, their well defined symmetries in the whole Racah group chain, and unambiguous time reversal symmetry.

The proof of the linear combinations of the operators o_i is the following. As shown in table 4.3, the one-body tensor operators $V^{(2)}$, $V^{(4)}$, $V^{(6)}$ ($V^{(1)}$, $V^{(3)}$, $V^{(5)}$)

together transform as the irrep [200] ([110]) of SO_7 and within the irrep $\langle 11\rangle$ ($\langle 2\rangle$) of Sp_{14}. The coefficients of linear combinations for each operator o_i can be written in the full Racah group chain as

$$\begin{aligned}
&(\{1;1\}\langle 11\rangle[200](20)kq : \{1;1\}\langle 11\rangle[200](20)kq' \,|\{11;11\}CWUKQ), \quad k=2,4,6\\
&(\{1;1\}\langle 2\rangle[110](11)kq : \{1;1\}\langle 2\rangle[110](11)kq' \,|\{11;11\}CWUKQ), \quad k=1,5 \qquad (4.32)\\
&(\{1;1\}\langle 2\rangle[110](10)kq : \{1;1\}\langle 2\rangle[110](10)kq' \,|\{11;11\}CWUKQ), \quad k=3
\end{aligned}$$

where $K=0, Q=0, q=-q'$, and C, W, U, K, and Q denote the irreps of Sp_{14}, SO_7, G_2, SO_3, and SO_2 respectively, and CWUK can only be

$$\begin{aligned}
\text{CWUK:}\quad & o_2 \quad \langle 0\rangle[000](00)0, && o_5 \quad \langle 22\rangle[111](00)0\\
& o_3 \quad \langle 1^4\rangle[220](22)0, && o_6 \quad \langle 22\rangle[220](22)0\\
& o_4 \quad \langle 22\rangle[000](00)0, && o_7 \quad \langle 22\rangle[400](40)0
\end{aligned}$$

Since these coefficients involve the irreps of U_{14} and Sp_{14} the complete calculation of these 3jm symbols has not been done; but we can still obtain some useful information about the structure of these linear combinations. For operators $V^{(k)}$ with k even (odd) transforming within the irrep $\langle 11\rangle$ ($\langle 2\rangle$) of Sp_{4l+2}, we have

$$\langle 11\rangle \otimes \{2\} = \langle 22\rangle + \langle 1^4\rangle + \langle 11\rangle + \langle 0\rangle, \qquad (4.33)$$

$$\langle 2\rangle \otimes \{2\} = \langle 4\rangle + \langle 22\rangle + \langle 11\rangle + \langle 0\rangle. \qquad (4.34)$$

Likewise at SO_7 group level we obtain

$$[200] \otimes \{2\} = [400] + [220] + [200] + [000], \qquad (4.35)$$

$$[110] \otimes \{2\} = [220] + [111] + [200] + [000]. \qquad (4.36)$$

The equations (4.33), (4.35) (4.34, 4.36) correspond to k even (k odd) $[V_i^{(k)}V_j^{(k)}]^{(0)}$ operators. The irreps $\langle 1^4\rangle$ and [400] only appear for such operators with k even and [111] with k odd. Hence we conclude that the operators o_3 and o_7 must be a linear combination of k even $[V_i^{(k)}V_j^{(k)}]^{(0)}$ (Coulomb) operators, and operator o_5 must be a linear combination of such with k odd (Trees) operators. Inspecting the symmetry properties of the operators e_i, we conclude that $o_3 = e_3$, $o_7 = e_2$, and $o_5 = e'_\beta$. The other operators, o_2, o_4, o_6, may be the linear combinations with k even and odd contributed by both the Coulomb terms and the Trees terms to these operators.

Since, more importantly, not only these scalar operators but also all the n-body orthogonal operators under our classification have well defined symmetry properties

within the Racah group chain and also have been classified according to their time reversal symmetry, we can apply the Wigner-Eckart theorem through the whole group chain to calculate the matrix elements of these n-body operators, especially when $n \geq 3$. For example, the matrix element of a time-even two-body operator o_7 within the f^2 state ^1D can be written as

$$\langle ^1D|o_7|^1D\rangle = (\{11\}\langle 11\rangle[200](20)2 : \{11\}\langle 11\rangle[200](20)2 \ |\{11;11\}\langle 22\rangle[400](40)0). \tag{4.37}$$

To calculate this matrix element completely we face the same technical problem as we have mentioned above in connection with eq. (4.33): a general and complete computer calculation remains to be done. Although the numerical or quantitative calculation is beyond the scope of this thesis, here we have given a general approach, general rules (time reversal selection rules), and associated group symmetry classification for many-body operators. Along with these discussions our results have tidied up the related literature. A calculational approach which draws on the power of the TRSRs for many-body interactions is an attractive project.

For example, by using the orthogonal operators we can now rewrite the matrix elements of the time-even two-body scalar operators (Coulomb and Trees operators) as the first-order approximation to the system Hamiltonian within the f^2 electron states as below in which the operators that may have non-zero matrix elements are given for each state.

^3P,	$\langle 11\rangle$ $^3[110](11)1$:	D_2o_2	$+0$	$+D_3o_3$	$+D_4o_4$	$+D_5o_5$	$+D_6o_6$
^3H,	$\langle 11\rangle$ $^3[110](11)5$:	D_2o_2	$+0$	$+D_3o_3$	$+D_4o_4$	$+D_5o_5$	$+D_6o_6$
^3F,	$\langle 11\rangle$ $^3[110](10)3$:	D_2o_2	$+0$	$+0$	$+D_4o_4$	$+D_5o_5$	$+0$
^1D,	$\langle 11\rangle$ $^1[200](20)2$:	D_2o_2	$+D_7o_7$	$+D_3o_3$	$+D_4o_4$	$+0$	$+D_6o_6$
^1G,	$\langle 11\rangle$ $^1[200](20)4$:	D_2o_2	$+D_7o_7$	$+D_3o_3$	$+D_4o_4$	$+0$	$+D_6o_6$
^1I,	$\langle 11\rangle$ $^1[200](20)6$:	D_2o_2	$+D_7o_7$	$+D_3o_3$	$+D_4o_4$	$+0$	$+D_6o_6$
^1S,	$\langle 0\rangle$ $^1[000](00)0$:	D_2o_2	$+0$	$+0$	$+0$	$+0$	$+0$

The operator D_1o_1 is neglected here since, first, o_1 belongs to unitary identity $\{0\}$, its matrix elements must equal to 1 for all states. Second, it is not orthogonal to $\hat{H}^{(0)}$ and could be absorbed into $\hat{H}^{(0)}$ to move the centre of gravity of the spectrum. The zero entries arise from selection rules on Kronecker products, and are in agreement with the TRSRs.

4.7 The branching rules for HT-even spin-dependent and HT-odd two-body operators

In the following Tables we give all branching rules of HT-even spin-dependent two-body and HT-odd two-body operators.

Table 4.7 Triplet HT-even fermion two-body operators $t(e)^{(1,K)}$

U_{14}	Sp_{14}	$SU_2 \times [SO(7)$	G(2)	SO(3)]	$t(e)_i^{(1,K)}$
$\{11;11\}$	$\langle 22\rangle$	$^3[310]$	(31)	$1,2,3^2,4,5^2,6^2,$	
				$7^2,8,9,10,11$	$t(e)_1^{(1,K)}$, $\langle 22\rangle^3[310](31)K$
			(30)	$1,3,4,5,6,7,9$	$t(e)_2^{(1,K)}$, $\langle 22\rangle^3[310](30)K$
			(21)	$2,3,4,5,7,8$	$t(e)_3^{(1,K)}$, $\langle 22\rangle^3[310](21)K$
		$^3[211]$	(30)	$1,3,4,5,6,7,9$	$t(e)_4^{(1,K)}$, $\langle 22\rangle^3[211](30)K$
			(21)	$2,3,4,5,7,8$	$t(e)_5^{(1,K)}$, $\langle 22\rangle^3[211](21)K$
			(20)	$2,4,6$	$t(e)_6^{(1,K)}$, $\langle 22\rangle^3[211](20)K$
			(11)	$1,5$	$t(e)_7^{(1,K)}$, $\langle 22\rangle^3[211](11)K$
			(10)	3	$t(e)_8^{(1,3)}$, $\langle 22\rangle^3[211](10)3$
		$^3[200]$	(20)	$2,4,6$	$t(e)_9^{(1,K)}$, $\langle 22\rangle^3[200](20)K$
		$^3[110]$	(11)	$1,5$	$t(e)_{10}^{(1,K)}$, $\langle 22\rangle^3[110](11)K$
			(10)	3	$t(e)_{11}^{(1,3)}$, $\langle 22\rangle^3[110](10)3$
	$\langle 1111\rangle$	$^3[211]$	(30)	$1,3,4,5,6,7,9$	$t(e)_{12}^{(1,K)}$, $\langle 1^4\rangle^3[211](30)K$
			(21)	$2,3,4,5,7,8$	$t(e)_{13}^{(1,3)}$, $\langle 1^4\rangle^3[211](21)K$
			(20)	$2,4,6$	$t(e)_{14}^{(1,K)}$, $\langle 1^4\rangle^3[211](20)K$
			(11)	$1,5$	$t(e)_{15}^{(1,K)}$, $\langle 1^4\rangle^3[211](11)K$
			(10)	3	$t(e)_{16}^{(1,3)}$, $\langle 1^4\rangle^3[211](10)3$
	$\langle 11\rangle$	$^3[110]$	(11)	$1,5$	$t(e)_{17}^{(1,K)}$, $\langle 11\rangle^3[110](11)K$
			(10)	3	$t(e)_{18}^{(1,3)}$, $\langle 11\rangle^3[110](10)3$

Table **4.8** Quintuplet HT-even fermion two-body operators $q(e)^{(2,K)}$

U_{14}	Sp_{14}	$SU_2 \times [SO(7)$	G(2)	SO(3)]	$q(e)_i^{(2,K)}$
$\{11;11\}$	$\langle 22\rangle$	$^5[220]$	(22)	0, 2, 4, 5, 6, 8, 10	$q(e)_1^{(2,K)}$, $\langle 22\rangle^5[220](22)K$
			(21)	2, 3, 4, 5, 7, 8	$q(e)_2^{(2,K)}$, $\langle 22\rangle^5[220](21)K$
			(20)	2, 4, 6	$q(e)_3^{(2,K)}$, $\langle 22\rangle^5[220](20)K$
		$^5[200]$	(20)	2, 4, 6	$q(e)_4^{(2,K)}$, $\langle 22\rangle^5[200](20)K$
		$^5[000]$	(00)	0	$q(e)_5^{(2,K)}$, $\langle 22\rangle^5[000](00)0$
	$\langle 1111\rangle$	$^5[111]$	(20)	2, 4, 6	$q(e)_6^{(2,K)}$, $\langle 1^4\rangle^5[111](20)K$
			(10)	3	$q(e)_7^{(2,K)}$, $\langle 1^4\rangle^5[111](10)3$
			(00)	0	$q(e)_8^{(2,0)}$, $\langle 1^4\rangle^5[111](00)0$

Table **4.9** Singlet HT-odd fermion two-body operators $s(o)^{(0,K)}$

U_{14}	Sp_{14}	$SU_2 \times [SO(7)$	G(2)	SO(3)]	$s(o)_i^{(0,K)}$
$\{11;11\}$	$\langle 211\rangle$	$^1[310]$	(31)	$1, 2, 3^2, 4, 5^2, 6^2,$	
				$7^2, 8, 9, 10, 11$	$s(o)_1^{(0,K)}$, $\langle 211\rangle^1[310](31)K$
			(30)	1, 3, 4, 5, 6, 7, 9	$s(o)_2^{(0,K)}$, $\langle 211\rangle^1[310](30)K$
			(21)	2, 3, 4, 5, 7, 8	$s(o)_3^{(0,K)}$, $\langle 211\rangle^1[310](21)K$
		$^1[211]$	(30)	1, 3, 4, 5, 6, 7, 9	$s(o)_4^{(0,K)}$, $\langle 211\rangle^1[211](30)K$
			(21)	2, 3, 4, 5, 7, 8	$s(o)_5^{(0,K)}$, $\langle 211\rangle^1[211](21)K$
			(20)	2, 4, 6	$s(o)_6^{(0,K)}$, $\langle 211\rangle^1[211](20)K$
			(11)	1, 5	$s(o)_7^{(0,K)}$, $\langle 211\rangle^1[211](11)K$
			(10)	3	$s(o)_8^{(0,3)}$, $\langle 211\rangle^1[211](10)3$
		$^1[110]$	(11)	1, 5	$s(o)_9^{(0,K)}$, $\langle 211\rangle^1[110](11)K$
			(10)	3	$s(o)_{10}^{(0,3)}$, $\langle 211\rangle^1[110](10)3$
	$\langle 11\rangle$	$^1[200]$	(20)	2, 4, 6	$s(o)_{11}^{(0,K)}$, $\langle 11\rangle^1[200](20)K$

Table 4.10 Triplet HT-odd fermion two-body operators $t(o)^{(1,K)}$

U_{14}	Sp_{14}	$SU_2 \times [SO(7)$	G(2)	SO(3)]	$t(o)_i^{(1,K)}$
$\{11;11\}$	$\langle 211\rangle$	$^3[310]$	(31)	$1,2,3^2,4,5^2,6^2,7^2$	
				$8,9,10,11$	$t(o)_1^{(1,K)}$, $\langle 211\rangle^3[310](31)K$
			(30)	$1,3,4,5,6,7,9$	$t(o)_2^{(1,K)}$, $\langle 211\rangle^3[310](30)K$
			(21)	$2,3,4,5,7,8$	$t(o)_3^{(1,K)}$, $\langle 211\rangle^3[310](21)K$
		$^3[220]$	(22)	$0,2,4,5,6,8,10$	$t(o)_4^{(1,K)}$, $\langle 211\rangle^3[220](22)K$
			(21)	$2,3,4,5,7,8$	$t(o)_5^{(1,K)}$, $\langle 211\rangle^3[220](21)K$
			(20)	$2,4,6$	$t(o)_6^{(1,K)}$, $\langle 211\rangle^3[220](20)K$
		$^3[211]$	(30)	$1,3,4,5,6,7,9$	$t(o)_7^{(1,K)}$, $\langle 211\rangle^3[211](30)K$
			(21)	$2,3,4,5,7,8$	$t(o)_8^{(1,K)}$, $\langle 211\rangle^3[211](21)K$
			(20)	$2,4,6$	$t(o)_9^{(1,K)}$, $\langle 211\rangle^3[211](20)K$
			(11)	$1,5$	$t(o)_{10}^{(1,K)}$, $\langle 211\rangle^3[211](11)K$
			(10)	3	$t(o)_{11}^{(1,3)}$, $\langle 211\rangle^3[211](10)3$
		$^3[200]$	(20)	$2,4,6$	$t(o)_{12}^{(1,K)}$, $\langle 211\rangle^3[200](20)K$
		$^3[111]$	(20)	$2,4,6$	$t(o)_{13}^{(1,K)}$, $\langle 211\rangle^3[111](20)K$
			(10)	3	$t(o)_{14}^{(1,3)}$, $\langle 211\rangle^3[111](10)3$
			(00)	0	$t(o)_{15}^{(1,0)}$, $\langle 211\rangle^3[111](00)0$
		$^3[110]$	(11)	$1,5$	$t(o)_{16}^{(1,K)}$, $\langle 211\rangle^3[110](11)K$
			(10)	3	$t(o)_{17}^{(1,3)}$, $\langle 211\rangle^3[110](10)3$
	$\langle 11\rangle$	$^3[110]$	(11)	$1,5$	$t(o)_{18}^{(1,K)}$, $\langle 11\rangle^3[110](11)K$
			(10)	3	$t(o)_{19}^{(1,3)}$, $\langle 11\rangle^3[110](10)3$

Table 4.11 Quintuplet HT-odd fermion two-body operators $q(o)^{(2,K)}$

U_{14}	Sp_{14}	$SU_2 \times [SO(7)$	G(2)	SO(3)]	$q(o)_i^{(2,K)}$
$\{11;11\}$	$\langle 211\rangle$	$^5[211]$	(30)	$1,3,4,5,6,7,9$	$q(o)_1^{(2,K)}$, $\langle 211\rangle^5[211](30)K$
			(21)	$2,3,4,5,7,8$	$q(o)_2^{(2,K)}$, $\langle 211\rangle^5[211](21)K$
			(20)	$2,4,6$	$q(o)_3^{(2,K)}$, $\langle 211\rangle^5[211](20)K$
			(11)	$1,5$	$q(o)_4^{(2,K)}$, $\langle 211\rangle^5[211](11)K$
			(10)	3	$q(o)_5^{(2,3)}$, $\langle 211\rangle^5[211](10)3$
		$^5[110]$	(11)	$1,5$	$q(o)_6^{(2,K)}$, $\langle 211\rangle^5[110](11)K$
			(10)	3	$q(o)_7^{(2,3)}$, $\langle 211\rangle^5[110](10)3$

CHAPTER 5

Perturbation Theory and Time Reversal Selection Rules

In chapters 3 and 4 we have discussed and obtained the time reversal selection rules imposed by hermitian conjugation and time reversal for general n-body spin-orbital tensor operators of the form $[\mathbf{w}_1^{(\kappa_1,k_1)}\mathbf{w}_2^{(\kappa_2,k_2)}\cdots\mathbf{w}_n^{(\kappa_n,k_n)}]_{\Pi,Q}^{(\Xi,K)}$. Since these tensor operators are a basis set, the selection rules are applicable to all n-body HT-even or HT-odd physical operators. The applications of earlier chapter were made to hermitian operators in the first order of perturbation. When establishing these rules (chapters 3 and 4) it was noted that a product of operators has its order reversed under hermitian conjugation. Until now this has not affected the resulting rules, since, first, the many-body operator must be symmetric under the permutation of any two-particle indices (see eq. 3.21), and second, the spin and orbital operators commute (see eq. 3.15).

However, complications arise in second-order perturbation. A certain Goldstone perturbation diagram corresponds to several terms with different ordering of physical operators. Each term may have a different energy denominator. The physical operators involved may or may not commute with each other. The TRSR appropriate for each diagram is modified accordingly. The discussion of section 3.5 is useful in some of these cases. To obtain a definite selection rule the operator or the effective operator in perturbation must have a well defined signature under the joint action of hermitian conjugation and time reversal. In section 5.1 a general analysis and discussion of the TRSRs associated with second-order perturbation effective operators have been given, in which all perturbation operators act on the same particle (the one-body case).

In practice, Judd-Ofelt theory (Judd 1962, Ofelt 1962) for intra-configurational $f^n - f^n$ transition intensities for lanthanide ions is just such a second-order pertur-

bation theory. The effects of the Laporte parity rule in restricting the direct role of odd-parity E1 operators such as $H_{A1} \equiv -e\mathbf{A}\cdot\mathbf{p}/m$, $H_E \equiv -e\mathbf{E}\cdot\mathbf{r}$ to interconfigurational transitions of (for lanthanides) the $f^n - f^{n-1}d$ type is well known (see e.g. section 6.2 of chapter 6). In Judd-Ofelt theory, another odd-parity coupling V_O, such as the appropriate part of a static ligand field, is added to provide the second $f^n - f^{n-1}d$ coupling and so to explain $f^n - f^n$ transitions in second-order of perturbation. Only the length gauge form of the matter-field interaction H_E is used in this theory. The two physical operators can be expressed in terms of the basis tensor operators: $H_E = \sum_{k_1,q_1} \mathbf{e}_{q_1} C^{(k_1)}_{q_1}$ with $k_1 = 1$ and $V_O = \sum_{k_2,q_2} B^{k_2}_{q_2} C^{(k_2)}_{q_2}$ with $k_2 = 1, 3, 5$. The basis operators $C^{k_1}_{q_1}$, $C^{k_2}_{q_2}$ may be coupled into an effective tensor operator $U^{(\lambda)}_\gamma$ with $\lambda \in k_1 \times k_2$, as introduced by Judd (1962) and Ofelt (1962). This has been discussed briefly in section 2.5. Judd and Ofelt proved that under certain approximations the rank λ of this coupled effective tensor operator is even. Over thirty years, this theory has been used for parameterised fittings of transition intensities for all of the lanthanide ions in various crystals and solutions and has been proved to be very successful. The inadequacy and the refinement of this theory to explain the spin-forbidden transitions are discussed by Wybourne (1968), Judd and Pooler (1982), Downer *et al.* (1988), Burdick *et al.* (1989), Burdick and Reid (1993), and Burdick, Kooy, and Reid (1993). In chapter 6 these spin-related problems will be discussed in more detail.

In section 5.2 the arguments used by Judd and Ofelt (1962) to obtain the even-rank rule for coupled tensor operators in their transition intensity theory in length gauge are reviewed and analysed in detail. By using the TRSR a more direct and strong restriction on the coupled spin-orbital ranks is obtained. For a TRSR to apply, the effective operator in perturbation must have a well defined HT signature. This usually requires equality of the energy denominators associated with palindromic reordering of component operators. The choice of equal energy denominators in the original Judd-Ofelt theory is guaranteed by palindromic symmetrisation/antisymmetrisation (without the closure); only the symmetric hermitian HT-even part of the real second-order perturbation matrix elements is retained. The validity of the omission of the anti-hermitian HT-odd part is verified in section 5.4 in which the gauge transformation of Judd-Ofelt theory also is discussed in the light of the TRSR associated with the discussion given in sections 5.1 and 5.3. A generalised discussion about the relationship between the even-rank (or odd-rank) rule used in Judd-Ofelt theory and

tensor cancellation selection rule is presented in section 5.3.

A discussion of TRSRs for the second-order Coulomb interaction and Trees' correction is given in section 5.5.

5.1 Second-order perturbation for one-body interaction and associated TRSRs

Let us discuss a general (one-body) second order perturbation matrix element

$$M_{gf}^{(2)} = \sum_i [\frac{\langle g|\hat{A}|i\rangle\langle i|\hat{B}|f\rangle}{\Delta E_i} + \frac{\langle g|\hat{B}|i\rangle\langle i|\hat{A}|f\rangle}{\Delta E_i'}], \tag{5.1}$$

where $\hat{A}$ and $\hat{B}$ are two one-body operators acting on the same particle, and ΔE and $\Delta E'$ may differ by a photon energy $\pm\hbar\omega$ if one of $\hat{A}$ and $\hat{B}$ is the matter-field interaction (see Moore and Stedman 1990). We define the *effective operator* $\hat{O}_e$ by

$$\hat{O}_e = \sum_i [\frac{\hat{A}|i\rangle\langle i|\hat{B}}{\Delta E_i} + \frac{\hat{B}|i\rangle\langle i|\hat{A}}{\Delta E_i'}]; \qquad M_{gf}^{(2)} = \langle g|\hat{O}_e|f\rangle, \tag{5.2}$$

so that the perturbation matrix element can be written as an *effective* operator $\hat{O}_e$ acting between the initial (g) and final (f) states. This definition of the *effective operator* is close to the definition of *effective Hamiltonian*, but is different from the *effective tensor operator* introduced in chapter 2 since, first, the angular part is not separated out; second, here the intermediate states i are retained in $\hat{O}_e$.

We can see that if and only if under the joint action HT $\hat{O}_e$ goes back to itself with a definite HT signature $\tau_e = \pm 1$ the original TRSR can be applied. Examining eq. (5.2) we note that, first, although $\hat{O}_e$ is written in a nearly symmetric form, if the energy denominators differ, it is not hermitian in this case. Second, the operators $\hat{A}$ and $\hat{B}$ may or may not commute. In section 3.5 an extension of TRSR has been made to a well defined anti-hermitian operator (see e.g. Messiah 1962) which involves two non-commutative hermitian operators forming a commutator such as $\mathbf{rp}-\mathbf{pr}$. As in section 3.5, $\hat{O}_e$ can be written as the sum of a hermitian and an anti-hermitian operator. In the anti-hermitian part, the non-commutative operators reduce to a commutator when the closure approximation (see eq. 5.10) is made.

Now let us discuss the HT symmetry of general second-order effective operators and associated TRSRs for various cases. First of all, we assume that the two terms in eq. (5.2) have the same energy denominators. In this case whether $\hat{A}$ and $\hat{B}$ commute

or not the $\hat{O}_e$ is hermitian. Under the joint action HT,

$$\begin{aligned}\overline{\hat{O}_e^\dagger} &= \sum_i [\frac{\overline{(\hat{A}|i\rangle\langle i|\hat{B})^\dagger}}{\Delta E_i} + \frac{\overline{(\hat{B}|i\rangle\langle i|\hat{A})^\dagger}}{\Delta E_i}] = \sum_i [\frac{\overline{\hat{A}^\dagger}|i\rangle\langle i|\overline{\hat{B}^\dagger}}{\Delta E_i} + \frac{\overline{\hat{B}^\dagger}|i\rangle\langle i|\overline{\hat{A}^\dagger}}{\Delta E_i}] \\ &= \tau_a\tau_b \sum_i [\frac{\hat{B}|i\rangle\langle i|\hat{A}}{\Delta E_i} + \frac{\hat{A}|i\rangle\langle i|\hat{B}}{\Delta E_i}] = \tau_a\tau_b\hat{O}_e = \tau_e\hat{O}_e, \end{aligned} \tag{5.3}$$

the perturbation effective one-body operator $\hat{O}_e$ has a well defined HT signature $\tau_e = \tau_a\tau_b$.

We now discuss the TRSRs associated with this effective operator. In tensorial form, two perturbation operators can be expressed in terms of the basis tensor operators as $\hat{A} \sim A^{(\kappa_1,k_1)}$ and $\hat{B} \sim B^{(\kappa_2,k_2)}$ where κ_i and k_i refer to the spin and orbital rank respectively. Eq. (5.3) is then written in an uncoupled tensorial form. The coupled tensor operators $\mathbf{W}^{(\kappa,k)}_{\pi,q}$ can be defined as

$$\begin{aligned}\mathbf{W}^{(\kappa,k)}_{\pi,q} &\equiv [A^{(\kappa_1,k_1)}B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q} \\ &\equiv \sum_{\pi_1,q_1,\pi_2,q_2} \begin{pmatrix} \kappa \\ \pi \end{pmatrix} \begin{pmatrix} \kappa_1 & \kappa_2 & \kappa \\ \pi_1 & \pi_2 & -\pi \end{pmatrix} \begin{pmatrix} k \\ q \end{pmatrix} \begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{pmatrix} A^{(\kappa_1,k_1)}_{\pi_1,q_1} B^{(\kappa_2,k_2)}_{\pi_2,q_2}, \end{aligned} \tag{5.4}$$

where the first (the second) 2jm and 3jm symbols correspond to the the coupling coefficient in the spin (orbital) space. In a physical application such as eq. (5.3), to couple two uncoupled tensor operators $A^{(\kappa_1,k_1)}$ and $B^{(\kappa_2,k_2)}$ one has to employ the orthogonality of the 3jm symbols, which involves a product of two 3j symbols for each coupling in each space. The intermediate state projection and the energy denominators in eq. (5.3) are invariant and will not affect this coupling. Thus the effective operator $\hat{O}_e$ can be expressed in terms of such coupled effective tensor operators as $\hat{O}_e \sim \mathbf{W}^{(\kappa,k)}_{\pi,q}$. In section 5.2 we will give more detailed accounts.

Under the joint action HT, such re-coupling in eq. (5.3) will not change the HT-signature of the effective operator $\hat{O}_e$. We still have $\overline{\hat{O}_e^\dagger} = \tau_e\hat{O}_e$ with $\tau_e = \tau_a\tau_b$. According to the one-body TRSR, eq. (3.29), the coupled spin-orbital ranks (κ, k) of $\mathbf{W}^{(\kappa,k)}_{\pi,q}$ are strictly restricted and we have

$$\tau_e = \tau_a\tau_b = (-1)^{\kappa+k}. \tag{5.5}$$

We conclude: *The sum of the coupled spin-orbital ranks $\kappa+k$ of an HT-even (HT-odd) effective one-body operator in perturbation must be even (odd) respectively.*

On the other hand, in this case, the component operators $A^{(\kappa_1,k_1)}$ and $B^{(\kappa_2,k_2)}$ are not restricted by any TRSR, since they do not act within a configuration.

Second, we consider the case that the two terms in eq. (5.2) have different energy denominators. This situation arise when one of the perturbation operators, say $\hat{A}$, is a matter-field interaction describing the optical absorption process such as the Judd-Ofelt one-photon absorption theory; or with two operators, $\hat{A}$ and $\hat{B}$, which are both matter-field interactions, one corresponds to absorption and another to emission such as Raman scattering. As discussed by Moore and Stedman (1990), palindromic symmetrisation of such a non-hermitian effective operator

$$\hat{O}_{e\pm} = \sum_i [\ (\hat{A}|i\rangle\langle i|\hat{B}) \pm (\hat{B}|i\rangle\langle i|\hat{A})\ ]\ C^i_\pm; \quad C^i_\pm = \frac{1}{2}(\frac{1}{\Delta E_i} \pm \frac{1}{\Delta E'_i}), \tag{5.6}$$

yields component operators $\hat{O}_{e+}$ and $\hat{O}_{e-}$ which are hermitian and anti-hermitian according to the definition given in section 3.5. Here, following the notation given in section 3.6, the superscripts $+,-$ are preserved for HT-even and HT-odd, and the subscripts $+,-$ for symmetrisation (hermitian) and anti-symmetrisation (anti-hermitian) respectively. Under the joint action HT we have:

$$\overline{(\hat{O}_{e+})^\dagger} = \tau_a\tau_b\hat{O}_{e+}; \qquad \overline{(\hat{O}_{e-})^\dagger} = -\tau_a\tau_b\hat{O}_{e-}. \tag{5.7}$$

Thus we will have not only a $\hat{O}_{e+}$ part (hermitian) with HT signature $\tau_{e+} = \tau_a\tau_b$, but also a $\hat{O}_{e-}$ part (anti-hermitian) with HT signature $\tau_{e-} = -\tau_a\tau_b$.

For the symmetrised hermitian part $\hat{O}_{e+}$ the associated TRSRs are exactly the same as in the previous case with equal denominators. We have

$$\tau_{e+} = \tau_a\tau_b = (-1)^{\kappa+k}. \tag{5.8}$$

The interpretation of this equation is the same as in the case of the same energy denominators: *For an hermitian HT-even (HT-odd) effective operators* O^+_{e+} (O^-_{e+}) *the sum of the coupled spin-orbital ranks* $\kappa + k$ *must be even (odd respectively).*

For the anti-hermitian part $\hat{O}_{e-}$ we have the same result,

$$\tau_{e-} = -\tau_a\tau_b = (-1)^{\kappa+k}. \tag{5.9}$$

We can interpret it as: *For an anti-hermitian HT-even (HT-odd) effective operators* O^+_{e-} (O^-_{e-}) *the sum of the coupled spin-orbital ranks* $\kappa + k$ *must be even (odd).*

In addition, under the strong closure approximation for the intermediate states,

$$\sum_i \frac{|i\rangle\langle i|}{\Delta E_i} \simeq \frac{1}{\Delta E}\sum_i |i\rangle\langle i| \simeq \frac{1}{\Delta E}, \tag{5.10}$$

the anti-hermitian part $\hat{O}_{e-}$ reduces to a commutator

$$\hat{O}_{e-} = [\hat{A}, \hat{B}]C_{-}. \tag{5.11}$$

If $\hat{A}$ and $\hat{B}$ commute, then it reduces to zero under strong closure.

Although the component operators are not restricted by the TRSR, we will show in section 5.3 that under certain approximations any effective operator in second-order perturbation written in the symmetrised ($\hat{O}_{e+}$) or antisymmetrised ($\hat{O}_{e-}$) form will be restricted by the *tensor cancellation rules* (see section 5.3 and eqns. 5.24, 5.26). This argument is in fact used by Judd (1962) and Ofelt (1962) to obtain their even-coupled-rank rule for their effective tensor operators. In section 5.3, on the other hand, we will show that since the final coupled spin-orbital ranks are restricted by one-body TRSR, the cancellation rule will lead to a restriction on the component operators, $A^{(\kappa_1,k_1)}$ and $B^{(\kappa_2,k_2)}$. The practical applications and discussion of these rules will be given in section 5.4.

5.2 Judd-Ofelt theory

As mentioned in the beginning of this chapter, Judd-Ofelt theory (Judd 1962, Ofelt 1962) of the intra-configurational transition intensities for lanthanide ions is a practical second-order perturbation theory. With the electric dipole operator written in terms of a rank 1 tensor operator $C^{(1)}$ and odd-parity crystal field written in terms of the odd rank $C^{(t)}$, under some approximations they obtained the well-known even-rank rule, i.e. the coupled effective tensor operators $U^{(\lambda)}$ have even rank λ. In a private communication Professor B. G. Wybourne (1992) commented: "*Judd (1962) remarks 'due to*

$$\begin{pmatrix} 1 & \lambda & t \\ q & -p-q & p \end{pmatrix} = (-1)^{1+\lambda+t} \begin{pmatrix} t & \lambda & 1 \\ p & -p-q & q \end{pmatrix}$$

the two parts cancel to a large extent if $1+\lambda+t$ *is odd.' λ is necessarily odd and hence Judd deduces that the approximate cancellation leaves only terms $U^{(\lambda)}$ with λ even. I have argued (Wybourne 1968, 1969) that if you start with a suitably defined Rayleigh-Schrödinger perturbation theory the cancellation is exact in second-order but then leave open the possibility of odd terms in third-order. It now seems to me that such (odd) terms should vanish to all orders of perturbation theory if one recognises that with k odd any one-body effective intensity operator will be time-odd and would*

correspond to an effective magnetic dipole operator and not an effective electric dipole operator. Perhaps you can sharpen up this argument and lay to rest this issue once and for all." These Judd-Ofelt effective tensor operator $U^{(\lambda)}$ can be treated as the coupled tensor operators of $C^{(1)}$ and $C^{(t)}$. We also note that, on the other hand, the physical applications, e.g. those perturbation equations (5.3) and (5.6) are written in the *uncoupled* form. To couple these uncoupled perturbation operators one has to employ the orthogonality of the 3jm symbols, which involve a product of two 3jm symbols. We could also ask how could one still obtain such an even-rank rule when each recoupling involves a product of two such 3jm symbols.

To answer these questions, we will re-derive Judd-Ofelt theory and review their argument in detail and compare with the result of the TRSR suitable for second-order perturbation, i.e. eqns. 5.7, 5.8, and 5.9. In chapter 2 (section 2.5) we have derived the Judd-Ofelt effective tensor operators in detail by using the angular momentum diagram method, in which special attention was paid to the simplified linkage between the Goldstone diagrams and the Jucys-type angular diagrams. Here we use it again and focus on the tensor coupling, the cancellation rule obtained by Judd and Ofelt (1962), and the relationship with the TRSR. Some content here may be repetitive in order to make our argument clear.

There are two physical operators appearing in Judd-Ofelt in second-order perturbation; $\hat{A} = H_E = -e\mathbf{E}\cdot\mathbf{r}$, the matter-field interaction in the length gauge, and $\hat{B} = V_O$, the odd-parity crystal field. Each operator can be expressed in terms of the basis tensor operators, $H_E = \sum_{k_1,q_1} \mathrm{e}_{q_1} C^{(k_1)}_{q_1}$ with $k_1 = 1$ and $V_O = \sum_{k_2,q_2} B^{k_2}_{q_2} C^{(k_2)}_{q_2}$ with $k_2 = 1,3,5$, where we use k_2 instead of λ to denote the tensor rank of V_O. A coupled effective tensor operator $U^{(\lambda)}_{\gamma}$ can be introduced as in the following. The matrix elements of such second-order perturbation terms can be written as

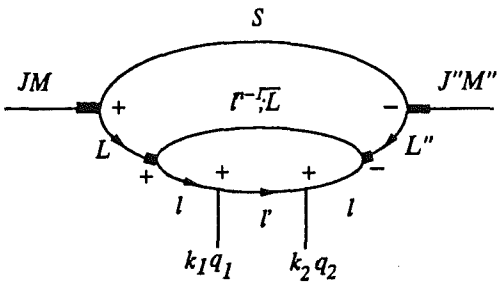
$$\sum[\frac{1}{E_f - E_i}\langle l^N SLJM_J|\mathrm{e}_{q_1} C^{(k_1)}_{q_1}|l^{N-1}l'SL'J'M'_J\rangle\langle l^{N-1}l'SL'J'M'_J|B^{k_2}_{q_2} C^{(k_2)}_{q_2}|l^N SL''J''M''_J\rangle$$

$$+ \frac{1}{E_g - E_i}(\mathrm{e}_{q_1} C^{(k_1)}_{q_1} \leftrightarrow B^{k_2}_{q_2} C^{(k_2)}_{q_2})] \simeq \sum \frac{1}{\Delta E}\,[\,\mathcal{M} + \mathcal{N}\,], \qquad (5.12)$$

where the E_g, E_i, and E_f correspond to the energy of the ground, intermediate, and the final state respectively, and $\mathcal{M}$ and $\mathcal{N}$ are abbreviations for the first and the second numerators, and the summation should run over all of intermediate states $|nl^{N-1}n'l'\alpha'SL'J'M'_J\rangle$, and k_1, q_1 and k_2, q_2. According to the discussion given in section 5.1 the formula $\frac{\mathcal{M}}{E_f - E_i} + \frac{\mathcal{N}}{E_g - E_i}$ can be written as the symmetrised part $\frac{1}{2}(\frac{1}{E_f - E_i} +$

$\frac{1}{E_g-E_i}$)$(\mathcal{M}+\mathcal{N})$ plus the antisymmetrised part $\frac{1}{2}(\frac{1}{E_f-E_i}-\frac{1}{E_g-E_i})(\mathcal{M}-\mathcal{N})$. The approximation in eq. (5.12) corresponds to the symmetrised hermitian part only. The states here are written in the Russell-Saunders coupling (LS-coupling) scheme of the N-electron states, e.g. $|nl^N\alpha SLJM_J\rangle$. A central field approximation for the zero-order Hamiltonian of the atomic system has been made. Since the one-body tensor operators $C^{(k_1)}$ and $C^{(k_2)}$ act within the same one-particle state only, the N-electron state must be factorised into an *(N-1)*-particle state and a one-particle state with an appropriate *fractional parentage coefficient* (cfp). The matrix element can be separated as a radial integral part, a reduced orbital part, and an angular part. Each angular momentum coupling in SO_3 is represented by a 3jm symbol with an appropriate phase. Calculating this matrix element involves all of the intermediate and unknown quantum numbers $n'l'$, L', J', and M'_J. Judd and Ofelt (1962) introduced the *effective tensor operator* which only acts between the initial state $\langle nl^N\alpha SLJM_J|$ and the final state $|nl^N\alpha''SL''J''M''_J\rangle$ which are in the same ground configuration nl^N. By doing so they introduce a *quasi-closure approximation* (weaker than eq. 5.10) which supposes that all of L', J' and M'_J are degenerate (see section 2.5). In return one can eliminate the intermediate quantum numbers L', J', M'_J and be left with only the angular quantum number l' of the excited configuration. Thus the first term $\sum\frac{\mathcal{M}}{\Delta E}$ of equation (5.12) can be written as

$$\sum\frac{\mathcal{M}}{\Delta E}=\sum\frac{1}{\Delta E}$$

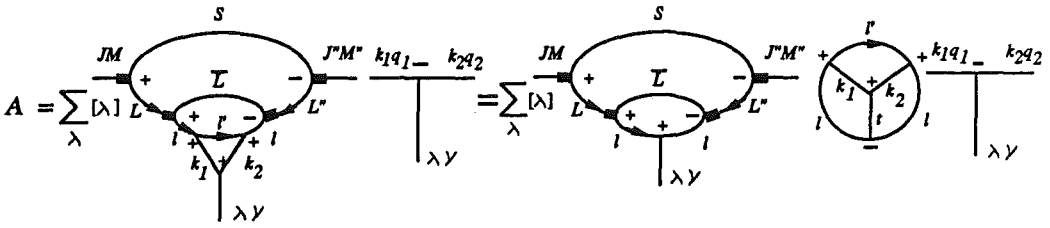


$$\times\ (l^NL\{|l^{N-1}\bar{L},l)(l^{N-1}\bar{L}'',l|\}l^NL'')\ (nl|r^{k_1}|n'l')(nl|r^{k_2}|n'l')(l||C^{(k_1)}||l')(l'||C^{(k_2)}||l). \tag{5.13}$$

Here the radial integral part is $(nl|r^{k_1}|n'l')(nl|r^{k_2}|n'l')$, the reduced orbital part is written as $(l||C^{(k_1)}||l')(l'||C^{(k_2)}||l)$, and the angular part is denoted by an angular-diagram associated with appropriate fractional parentage coefficients which are denoted as $(l^NL\{|l^{N-1}\bar{L},l)$ and $(l^{N-1}\bar{L}'',l|\}l^NL'')$. The Jucys-type angular momentum coupling diagram (SO_3) is used, and the phase conventions (arrows, $+/-$ signs) are in agreement with Lindgren and Morrison (1982).

The next step is to apply the unitarity of the 3jm symbols which can be used to

"pinch" the k_1 and k_2 lines and to form a λ line. Applying JLV3 for two l lines and a λ line, thus a 6j symbol can be separated out. We obtain



A matrix element of the *effective tensor operator* $U_\gamma^{(\lambda)}$ is defined as the first diagram on the right-hand-side of the above diagram "equation" with appropriate cfp's as

$$\begin{aligned}
&\langle l^N \alpha SLJM_J | U_\gamma^{(\lambda)} | l^N \alpha'' SL''J''M_J'' \rangle \\
&\quad = [L, J, L'', J'']^{1/2} \sum_{\bar{L}} (l^N L \{ | l^{N-1} \bar{L}, l)(l^{N-1} \bar{L}'', l | \} l^N L'')(-1)^{2S+L+L''+J''+\lambda} \\
&\quad \times \begin{Bmatrix} J & J'' & \lambda \\ L'' & L & S \end{Bmatrix} \begin{Bmatrix} L & L'' & \lambda \\ l & l & \bar{L} \end{Bmatrix} \begin{pmatrix} J & \lambda & J'' \\ M_J & -\gamma & M_J'' \end{pmatrix}.
\end{aligned} \tag{5.14}$$

For detailed derivation of this equation one can refer to section 2.5.

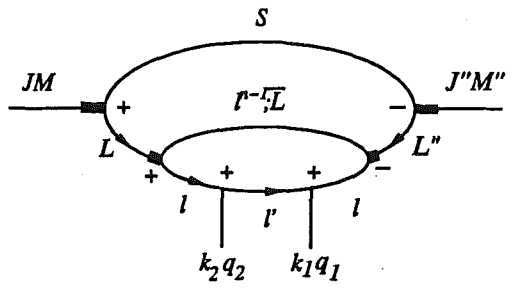
Finally the first term, $\sum \frac{\mathcal{M}}{\Delta E}$, in eq. (5.12) can be written algebraically as

$$\begin{aligned}
\sum \frac{\mathcal{M}}{\Delta E} \;=\; & \sum_{n',l'} \frac{1}{\Delta E} \sum_{k_1,k_2,q_1,q_2} \mathrm{e}_{q_1} B_{q_2}^{k_2} (nl|r^{k_1}|n'l')(nl|r^{k_2}|n'l')(l||C^{(k_1)}||l')(l'||C^{(k_2)}||l) \\
& \times \sum_\lambda [\lambda](-1)^\lambda \begin{Bmatrix} k_1 & k_2 & \lambda \\ l & l & l' \end{Bmatrix} \begin{pmatrix} k_1 & \lambda & k_2 \\ q_1 & -\gamma & q_2 \end{pmatrix} \\
& \times \langle l^N \alpha SLJM_J | U_\gamma^{(\lambda)} | l^N \alpha'' SL''J''M_J'' \rangle.
\end{aligned} \tag{5.15}$$

This result is in agreement with Judd (1962) and Ofelt (1962). We can see that the effective tensor operator $U_\gamma^{(\lambda)}$ is a coupled tensor operator from $C_{q_1}^{(k_1)}$ and $C_{q_2}^{(k_2)}$. Thus the angular parts of uncoupled second-order perturbation operators can form coupled tensor operators through the application of the orthogonality of 3jm symbols.

Now let us discuss the second term, $\sum \frac{\mathcal{N}}{\Delta E}$, in eq. (5.12). In this term the order of two interaction operators is reversed. Thus the ranks k_1 and k_2 are swapped in corresponding angular diagram and it can be written as

$$\sum \frac{\mathcal{N}}{\Delta E} = \sum \frac{1}{\Delta E}$$



$$\times\ (l^N L\{|l^{N-1}\bar{L}, l)(l^{N-1}\bar{L}'', l|\}l^N L'')\ (nl|r^{k_2}|n'l')(nl|r^{k_1}|n'l')(l||C^{(k_2)}||l')(l'||C^{(k_1)}||l). \tag{5.16}$$

Again, by using the same angular diagram technique, the angular part of eq. (5.16) can be manipulated in the same manner as before. Eq. (5.16) can then be written algebraically as

$$\begin{aligned}\sum \frac{\mathcal{N}}{\Delta E} \;=\; & \sum_{n',l'} \frac{1}{\Delta E} \sum_{k_1,k_2,q_1,q_2} \mathbf{e}_{q_1} B^{k_2}_{q_2}(nl|r^{k_2}|n'l')(nl|r^{k_1}|n'l')(l||C^{(k_2)}||l')(l'||C^{(k_1)}||l) \\ & \times \sum_{\lambda}[\lambda](-1)^{\lambda} \begin{Bmatrix} k_2 & k_1 & \lambda \\ l & l & l' \end{Bmatrix} \begin{pmatrix} k_2 & \lambda & k_1 \\ q_2 & -\gamma & q_1 \end{pmatrix} \\ & \times \langle l^N \alpha S L J M_J | U^{(\lambda)}_{\gamma} | l^N \alpha'' S L'' J'' M''_J \rangle. \end{aligned} \tag{5.17}$$

Comparing $\sum \frac{\mathcal{N}}{\Delta E}$ (eq. 5.17) with $\sum \frac{\mathcal{M}}{\Delta E}$ (eq. 5.15), first, although the k_1 and k_2 are swapped in the 6j symbol in the first term, but it is the same as the 6j symbol in the second since such a column permutation is a symmetry operation for a 6j symbol. Second, the radial integrals for these two terms are different. However, this difference is removed by the approximation (see Judd 1962) that

$$\sum_{n'}(nl|r^{k_1}|n'l')(nl|r^{k_2}|n'l') \;\simeq\; (nl|r^{k_1+k_2}|nl). \tag{5.18}$$

Third, the reduced matrix elements for these two equations are identical, since these reduced matrix elements by definition (Judd 1963) are

$$\begin{aligned}(l||C^{(k_1)}||l')(l'||C^{(k_2)}||l) \;&=\; (-1)^{l+l'}[l][l'] \begin{pmatrix} l & k_1 & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & k_2 & l \\ 0 & 0 & 0 \end{pmatrix}, \\ (l||C^{(k_2)}||l')(l'||C^{(k_1)}||l) \;&=\; (-1)^{l+l'}[l][l'] \begin{pmatrix} l & k_2 & l' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & k_1 & l \\ 0 & 0 & 0 \end{pmatrix}, \end{aligned} \tag{5.19}$$

and the sum of the ranks in each of these 3jm symbols must be even for the 3jm symbol to be non-zero. Judd has popularized the view that one starts from this 3jm

rule to derive the result on reduced matrix elements. Thus these special 3jm symbols are symmetric under column permutation and the reduced matrix elements for two equations are the same. We note that such an argument based on the even-rank rule for such 3jm symbols employs the Derome-Sharp lemma, i.e. the behaviour of the 3jm symbols under time reversal (or complex conjugation) so that its use here or as in Judd-Ofelt to derive the even rank rule amounts to the use of a time reversal symmetry argument (see Stedman 1987). We would also emphasize that an argument based only on an examination of rank cannot lead by itself to a selection rule (such as the various rules for "hermiticity", see chapter 3 and also Wang and Stedman 1992a,b) or the Judd-Ofelt restriction to even ranks, without also invoking time reversal.

To this end, the only difference between that two equations is the difference of two general 3jm symbols. Thus, all together, right-hand-side of eq. (5.12) can be finally written as

$$\sum \frac{\mathcal{M}+\mathcal{N}}{\Delta E} = \sum_{l'} \frac{1}{\Delta E} \sum_{k_1,k_2,q_1,q_2} \mathbf{e}_{q_1} B^{k_2}_{q_2} (nl|r^{k_1+k_2}|nl)(l||C^{(k_1)}||l')(l'||C^{(k_2)}||l)$$
$$\times \sum_{\lambda} [\lambda](-1)^{\lambda} \begin{Bmatrix} k_1 & k_2 & \lambda \\ l & l & l' \end{Bmatrix} [\begin{pmatrix} k_1 & \lambda & k_2 \\ q_1 & -\gamma & q_2 \end{pmatrix} + \begin{pmatrix} k_2 & \lambda & k_1 \\ q_2 & -\gamma & q_1 \end{pmatrix}]$$
$$\times \langle l^N \alpha S L J M_J | U^{(\lambda)}_{\gamma} | l^N \alpha'' S L'' J'' M''_J \rangle. \qquad (5.20)$$

Therefore Judd concluded: "*the two parts cancel to a large extent if* $1+\lambda+t$ *(*$k_1+\lambda+k_2$ *in the above equation) is odd.* $\cdots$ t *(i.e.* k_2*) must be odd; hence the (cancellation) condition is fulfilled if* λ *is odd. The cancellation would be perfect if, or a given* n' *and* l' *(intermediate configuration), the energy denominators*

$$E(\psi J) - E(n'l', \psi'' J'') \quad \rightarrow \quad (E_g - E_i)$$
$$E(\psi' J') - E(n'l', \psi'' J'') \quad \rightarrow \quad (E_f - E_i)$$

which are supposed to be independent of ψ'' *and* J'' *(a weaker closure approximation), could be assumed equal. This is equivalent to the supposition that the (intermediate) configuration* $l^{N-1}n'l'$ *lie far above the states involved in the optical transitions.*" This approximation of equating two energy denominators in the left-hand-side of eq. (5.12) has the effect of omitting the antisymmetrised part. Thus this approximation with other approximations discussed above lead to the result that the rank λ of the effective tensor operator $U^{(\lambda)}_{\gamma}$ can only be even. This effective tensor operator $U^{(\lambda)}_{\gamma}$ is a coupled tensor operator from two uncoupled operators $C^{(k_1)}_{q_1}$ and $C^{(k_2)}_{q_2}$. In the next section, we can generalise this conclusion.

On the other hand, by using a one-body TRSR, eq. (5.5) or eq. (5.8) we can easily reach the same conclusion but without the use of the closure approximation. Since the effective operator in the right-hand-side of eq. (5.12) is

$$\begin{aligned} O_{E+} &= \sum \frac{1}{\Delta E}[\mathrm{e}_{q_1} C^{(k_1)}_{q_1} |l^{N-1}l', SL'J'M'_J\rangle\langle l^{N-1}l', SL'J'M'_J| B^{k_2}_{q_2} C^{(k_2)}_{q_2} \\ &\quad + B^{k_2}_{q_2} C^{(k_2)}_{q_2} |l^{N-1}l', SL'J'M'_J\rangle\langle l^{N-1}l', SL'J'M'_J| \mathrm{e}_{q_1} C^{(k_1)}_{q_1}], \end{aligned} \tag{5.21}$$

which corresponds to the symmetrised hermitian part of the real second-order perturbation, the left-hand-side of eq. (5.12). For this O_{E+} part, its HT signature is even. Therefore according to eqns. (5.5) or (5.8) the coupled orbital ranks can only be even (the spin rank is zero in this case) to have a non-zero matrix element without invoking the closure approximation. This restriction is strict and needs neither of the approximations made by Judd and Ofelt (closure approximation and equal radial integrals approximation); nor does it need explicit examination of particular 3jm symbols.

Up to here, we can only partially answer Wybourne's question. If we only discuss the symmetrised hermitian part O_{E+}, according to the TRSR (eq. 5.5) O_{E+} can only have *even* coupled spin-orbital ranks simply because the two physical operators H_E and V_O are both time-even, the symmetrised form of Judd-Ofelt formulation is hermitian under H, and thus the whole effective operator O_E is HT-even. However, on the contrary, if one considers the antisymmetrised (anti-hermitian) part O_{E-}, since the HT signature of O_{E-} is odd, it can only have *odd* coupled spin-orbital ranks.

5.3 Tensor cancellation selection rules

By inspecting eq. (5.20) the even-rank rule is obtained by Judd and Ofelt by noting the difference between two 3jm symbols which are the tensor coupling coefficients. For simplicity we may omit the intermediate states and the energy denominators since they will not affect the tensor coupling. Let us imagine, in a more general case, that the operator is

$$O_+ = [A^{(\kappa_1,k_1)} B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q} + [B^{(\kappa_2,k_2)} A^{(\kappa_1,k_1)}]^{(\kappa,k)}_{\pi,q}, \tag{5.22}$$

where

$$[A^{(\kappa_1,k_1)} B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q} \equiv \sum_{\pi_1,q_1,\pi_2,q_2} \begin{pmatrix} \kappa \\ \pi \end{pmatrix} \begin{pmatrix} \kappa_1 & \kappa_2 & \kappa \\ \pi_1 & \pi_2 & -\pi \end{pmatrix} \begin{pmatrix} k \\ q \end{pmatrix} \begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{pmatrix} A^{(\kappa_1,k_1)}_{\pi_1,q_1} B^{(\kappa_2,k_2)}_{\pi_2,q_2},$$

$$[B^{(\kappa_2,k_2)}A^{(\kappa_1,k_1)}]^{(\kappa,k)}_{\pi,q} \equiv$$
$$\sum_{\pi_1,q_1,\pi_2,q_2} \begin{pmatrix} \kappa \\ \pi \end{pmatrix} \begin{pmatrix} \kappa_2 & \kappa_1 & \kappa \\ \pi_2 & \pi_1 & -\pi \end{pmatrix} \begin{pmatrix} k \\ q \end{pmatrix} \begin{pmatrix} k_2 & k_1 & k \\ q_2 & q_1 & -q \end{pmatrix} B^{(\kappa_2,k_2)}_{\pi_2,q_2} A^{(\kappa_1,k_1)}_{\pi_1,q_1}.$$

$A^{(\kappa_1,k_1)}$ and $B^{(\kappa_2,k_2)}$ represent two physical operators $\hat{A}$ and $\hat{B}$ respectively. If these two physical operators commute, $[\hat{A},\hat{B}] = 0$, the uncoupled tensor operators also commute, $A^{(\kappa_1,k_1)}_{\pi_1,q_1} B^{(\kappa_2,k_2)}_{\pi_2,q_2} = B^{(\kappa_2,k_2)}_{\pi_2,q_2} A^{(\kappa_1,k_1)}_{\pi_1,q_1}$. Thus we have

$$\begin{aligned} O_+ &= [A^{(\kappa_1,k_1)}B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q} + [B^{(\kappa_2,k_2)}A^{(\kappa_1,k_1)}]^{(\kappa,k)}_{\pi,q} \\ &= \sum_{\pi_1 q_1,\pi_2 q_2} \begin{pmatrix} \kappa \\ \pi \end{pmatrix} \begin{pmatrix} k \\ q \end{pmatrix} [\begin{pmatrix} \kappa_1 & \kappa_2 & \kappa \\ \pi_1 & \pi_2 & -\pi \end{pmatrix} \begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{pmatrix} \\ &\quad + \begin{pmatrix} \kappa_2 & \kappa_1 & \kappa \\ \pi_2 & \pi_1 & -\pi \end{pmatrix} \begin{pmatrix} k_2 & k_1 & k \\ q_2 & q_1 & -q \end{pmatrix}] A^{(\kappa_1,k_1)}_{\pi_1,q_1} B^{(\kappa_2,k_2)}_{\pi_2,q_2} \\ &= [1+(-1)^{\kappa_1+\kappa_2+k_1+k_2+\kappa+k}][A^{(\kappa_1,k_1)}B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q}. \end{aligned} \tag{5.23}$$

Thus we obtain a tensor cancellation rule: *if the sum over coupled plus uncoupled spin-orbital ranks is odd, the palindromic symmetrised coupled operator O_+ will be zero, the two terms cancelling each other.* This simple new tensor coupling condition independent of time reversal is adequate to prove this cancellation rule (eq. 5.23). Indeed, this philosophy is evident in the Judd-Ofelt rule. To obtain this simple result here we start with the coupled tensor operators. We note that in fact, the physical applications in perturbation are in the *uncoupled form* (see e.g. eqns. 5.12, 5.21). To couple those uncoupled operators one has to employ the orthogonality of the 3jm symbols (i.e. "pinching" two lines used in the last section) which involves a product of two 3jm symbols for each coupling in each space. Under certain approximations discussed in section 5.2, the difference in two palindromic symmetrised perturbation terms (see eq. 5.20) is two 3jm symbols (in orbital space only) which is the same as in eq. (5.23).

Now we complement this cancellation rule from another angle, the TRSR. We know from section 5.1 that the coupled spin-orbital ranks (κ, k) are restricted by the one-body TRSR, i.e. $\kappa + k$ must be even (odd) for HT-even (HT-odd) operators. Due to this TRSR plus the tensor cancellation rule (see eq. 5.23), we can rewrite eq. (5.23) as

$$O^{\pm}_{+} \simeq [1 \pm (-1)^{\kappa_1+\kappa_2+k_1+k_2}][A^{(\kappa_1,k_1)}B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q} \tag{5.24}$$

where the superscript + (−) refers to HT-even (HT-odd respectively), and ≃ indicates that in physical application this relationship only holds under certain approximations. Hence, we conclude: *for an HT-even (HT-odd) palindromic symmetrised operator* O_+^+ *(*O_+^-*),* $\kappa_1+\kappa_2+k_1+k_2$*, the sum of the spin-orbital ranks of the component operators should be even (odd) to have non-zero (no cancellation) effect.*

We can also extend this argument to palindromic antisymmetrised operator O_-;

$$\begin{aligned} O_- &\simeq [A^{(\kappa_1,k_1)}B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q} - [B^{(\kappa_2,k_2)}A^{(\kappa_1,k_1)}]^{(\kappa,k)}_{\pi,q} \\ &\simeq [1-(-1)^{\kappa_1+\kappa_2+k_1+k_2+\kappa+k}][A^{(\kappa_1,k_1)}B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q}. \end{aligned} \tag{5.25}$$

By the same token, similar to eq. (5.24), according the one-body TRSR we obtain

$$O_-^{\pm} \simeq [1 \mp (-1)^{\kappa_1+\kappa_2+k_1+k_2}][A^{(\kappa_1,k_1)}B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q}. \tag{5.26}$$

Thus we reach the conclusion: *for an HT-even (HT-odd) palindromic antisymmetrised operator* O_-^+ *(*O_-^-*),* $\kappa_1+\kappa_2+k_1+k_2$*, the sum of the spin-orbital ranks of the component operators should be odd (even) to have non-zero (no cancellation) effect.*

These results, eqns. (5.24), (5.26), combining the considerations of the TRSR and the tensor cancellation rule are new, and they will be used in practical applications discussed in the next section and in chapter 6. We also noted that if two physical operators do not commute, one can obtain no rule at all by using the same tensor coupling arguments. On the other hand, the TRSRs (eqns. 5.8 and 5.9), which associated with symmetrised and antisymmetrised tensor operators in coupled form, are still valid even if two physical operators do not commute.

Besides, the even-rank rule obtained by Judd and Ofelt sometimes gives the impression that this rule will *restrict* the tensor coupling in a single term. Apparently this is not the case. It is not true at all to say that two odd-ranked operators (with ranks k_1 (odd) and k_2 (odd)) cannot couple to odd ranks in a single term. We choose $\hat{A} = \mathbf{s}$ and $\hat{B} = \mathbf{r}$ as an example. These two rank 1 commuting operators *can* couple to all possible ranks, $k = 0, 1, 2$ in a single term, e.g. $\mathbf{s}\cdot\mathbf{r} \neq 0$ and $\mathbf{s}\times\mathbf{r} \neq 0$. But in a palindromic symmetric form, $\mathbf{s}\cdot\mathbf{r}+\mathbf{r}\cdot\mathbf{s} \neq 0$, $\mathbf{s}\times\mathbf{r}+\mathbf{r}\times\mathbf{s} = 0$. The case of $\mathbf{s}\times\mathbf{r}+\mathbf{r}\times\mathbf{s} = 0$ is in agreement with the cancellation selection rule.

5.4 Gauge-transformed Judd-Ofelt theory

Now we discuss gauge transformation in the Judd-Ofelt theory. In the length gauge, the effective operator used by Judd and Ofelt (1962) within f^N has the form (left-

hand-side of eq. 5.12):

$$O_E = -\sum_i [\frac{H_E|i\rangle\langle i|V_O}{(E_f - E_i)} + \frac{V_O|i\rangle\langle i|H_E}{(E_g - E_i)}]. \tag{5.27}$$

We have pointed out in section 5.2 that Judd-Ofelt theory gives only the symmetrised part O_{E+} when the energy denominators in this equation are equated. In section 5.2, a detailed derivation of the evenness of the orbital ranks of the coupled effective tensor operators in Judd-Ofelt theory has been given. We have also shown that the TRSRs (eqns. 5.8 and 5.9) give a direct and strict restriction on these coupled spin-orbital ranks.

On the other hand, it has been assumed for a long time that in the E1 limit, the matter-field interaction operator in the velocity gauge $H_A = -e\mathbf{A}\cdot\mathbf{p}/m + e^2\mathbf{A}^2/2m$ is equivalent to $H_E = -e\mathbf{E}\cdot\mathbf{r}$ in the length gauge. In general, as we will discuss in section 6.2 of chapter 6, this statement is true only under certain conditions. Here we assume all such conditions are satisfied to make H_A and H_E equivalent, and we only discuss the gauge transformation property of the Judd-Ofelt theory in this sense. In addition, for the sake of simplicity, we will also ignore the non-local character of the Hartree-Fock potential which may lead to some complication under gauge transformation (see e.g. Reid 1988).

Our first remark is that from the perspective of the time-reversal selection rules, the Judd-Ofelt formalism might be expected to show a strong gauge dependence. The electronic momentum and position operators $\mathbf{p}$, $\mathbf{r}$ have opposite character under time reversal, being time-odd and time-even respectively. Apparently, if one keeps the Judd-Ofelt approach but simply changes H_E to the linear part of H_A, $H_{A1} = -e\mathbf{A}\cdot\mathbf{p}/m$, in the symmetrised part O_{A+}, the result would be the same – an even-rank rule. That will contradict with the TRSR discussed in section 5.1 (see eqns. 5.8 and 5.9). To understand this problem we must re-analyse the Judd-Ofelt-type second-order theory in the two different gauges systematically. By taking the effect of different energy denominators into account fully and using the TRSRs discussed in section 5.1 and the tensor cancellation rules discussed in section 5.3 a reconciliation of the Judd-Ofelt even-rank rule in two gauges could be recovered.

Replacing H_E by H_{A1} in eq. (5.27), the Judd-Ofelt theory can be written in the velocity gauge as

$$O_A = -\sum_i [\frac{H_{A1}|i\rangle\langle i|V_O}{(E_f - E_i)} + \frac{V_O|i\rangle\langle i|H_{A1}}{(E_g - E_i)}]. \tag{5.28}$$

In the case of the parity rule, it is the vectorial (odd parity) nature of the electronic operators **r**, **p** in the length and velocity gauge interactions H_E, H_{A1} which preclude their intraconfigurational coupling. According to the time reversal selection rule (see eq. 5.7, it is the time reversal signature which determines whether or not the operator in question can have matrix elements within a configuration. The effective operator O_A obtained in the velocity gauge is predominantly time-odd, since the electronic operators in H_{A1} is time-odd while the corresponding electronic operator in H_E is time-even. It is in the (relatively good) "degeneracy" approximation when $\Delta_i \gg \hbar\omega$ that this sign will also be the HT signature of H_{A1}, H_E themselves, and so will restrict their matrix elements to odd and even coupled ranks respectively. In particular, O_A (eq. 5.28) cannot contribute to an intraconfigurational orbital matrix element in the degenerate limit ($\omega \to 0$).

We give a more detailed analysis, related to those of Malta (1982) and Reid (1988) who discuss Judd-Ofelt theory in the velocity gauge, also Moore and Stedman (1990) (see section 5.1) who show explicitly and in general how an effective operator of such a type will have HT-even and HT-odd parts. We can distinguish the HT-even and HT-odd parts in both the velocity and length gauge as

$$O^{\pm}_{A\mp} = -\frac{1}{2}\sum_i [H_{A1}|i\rangle\langle i|V_O \mp V_O|i\rangle\langle i|H_{A1}][\frac{1}{(\Delta-\hbar\omega)} \mp \frac{1}{\Delta}], \tag{5.29}$$

$$O^{\pm}_{E\pm} = -\frac{1}{2}\sum_i [H_E|i\rangle\langle i|V_O \pm V_O|i\rangle\langle i|H_E][\frac{1}{(\Delta-\hbar\omega)} \pm \frac{1}{\Delta}], \tag{5.30}$$

where $\Delta = E_g - E_i$ and we keep use the same notation for the superscript/subscript $\pm$ as before. HT-even O^+_{A-} (HT-odd O^-_{A+}) part corresponds to an anti-hermitian and time-odd (hermitian and time-odd respectively) operator; HT-even O^+_{E+} (HT-odd O^-_{E-}) part corresponds to an hermitian and time-even operator (anti-hermitian and time-even respectively).

According to the TRSRs discussed in section 5.1 (eqns. 5.8 and 5.9) which related to the perturbation effective operator in the case of two different energy denominators, we have

$$\tau_{e\pm} = \pm\tau_a\tau_b = (-1)^{\kappa+k}, \tag{5.31}$$

where κ and k are the spin-orbital ranks of coupled effective tensor operators. According to the discussion given in section 5.3, we also have the tensor cancellation rules, eqns. (5.24) and (5.26)

$$O^{\pm}_{+} \simeq [1 \pm (-1)^{\kappa_1+\kappa_2+k_1+k_2}][A^{(\kappa_1,k_1)}B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q} \tag{5.32}$$

$$O^{\pm}_{-} \simeq [1 \mp (-1)^{\kappa_1+\kappa_2+k_1+k_2}][A^{(\kappa_1,k_1)}B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q}. \tag{5.33}$$

First, we discuss the HT-odd part in two different gauges,

$$O^{-}_{A+} = -\frac{1}{2}\sum_i [H_{A1}|i\rangle\langle i|V_O + V_O|i\rangle\langle i|H_{A1}][\frac{1}{(\Delta-\hbar\omega)} + \frac{1}{\Delta}] \tag{5.34}$$

$$O^{-}_{E-} = -\frac{1}{2}\sum_i [H_E|i\rangle\langle i|V_O - V_O|i\rangle\langle i|H_E][\frac{1}{(\Delta-\hbar\omega)} - \frac{1}{\Delta}]. \tag{5.35}$$

According to eq. (5.31), these two HT-odd operators can have only *odd* coupled orbital ranks. This is a general result and is not dependent on a closure approximation.

In addition, according to the tensor cancellation rules, eq. (5.32), under the closure approximation, for O^{-}_{A+} part (palindromic symmetrised and HT-odd part) we have

$$O^{-}_{A+} \simeq [1 - (-1)^{\kappa_1+\kappa_2+k_1+k_2}][A^{(\kappa_1,k_1)}B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q}. \tag{5.36}$$

Since for component spin-orbital ranks $\kappa_1 = \kappa_2 = 0$, and $k_1 + k_2$ (the sum of the orbital ranks of H_{A1} and V_O) is even, there is a near cancellation for O^{-}_{+}. For O^{-}_{E-} part (palindromic antisymmetrised and HT-odd part), according to eq. (5.33) we have

$$O^{-}_{E-} \simeq [1 + (-1)^{\kappa_1+\kappa_2+k_1+k_2}][A^{(\kappa_1,k_1)}B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q}. \tag{5.37}$$

From this equation, under closure approximation, the near cancellation condition requires $k_1 + k_2$ to be odd. This condition is not satisfied by H_E and V_O. However, under similar closure approximation, O^{-}_{E} reduces to a commutator; and H_E and V_O commute. Thus both O^{-}_{A+} and O^{-}_{E-} tend to be zero.

Second, we consider the HT-even part in two gauges. They are

$$O^{+}_{A-} = -\frac{1}{2}\sum_i [H_{A1}|i\rangle\langle i|V_O - V_O|i\rangle\langle i|H_{A1}][\frac{1}{(\Delta-\hbar\omega)} - \frac{1}{\Delta}], \tag{5.38}$$

$$O^{+}_{E+} = -\frac{1}{2}\sum_i [H_E|i\rangle\langle i|V_O + V_O|i\rangle\langle i|H_E][\frac{1}{(\Delta-\hbar\omega)} + \frac{1}{\Delta}]. \tag{5.39}$$

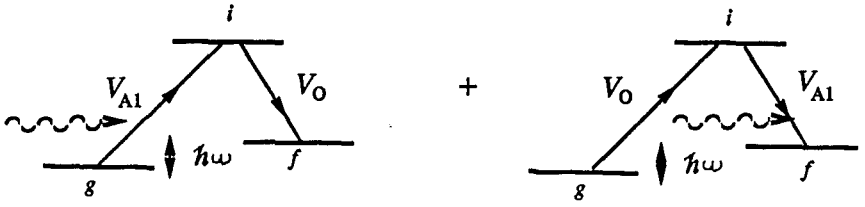
They can have only the *even* coupled ranks according to the eq. (5.31). We note that under the closure approximation, according to eq. (5.32), there will have no cancellation between two terms of O^{+}_{E+};

$$O^{+}_{E+} \simeq [1 + (-1)^{\kappa_1+\kappa_2+k_1+k_2}][A^{(\kappa_1,k_1)}B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q}. \tag{5.40}$$

But O^{+}_{A-} do satisfy the near cancellation requirement of eq. (5.33) under the same condition

$$O^{+}_{A-} \simeq [1 - (-1)^{\kappa_1+\kappa_2+k_1+k_2}][A^{(\kappa_1,k_1)}B^{(\kappa_2,k_2)}]^{(\kappa,k)}_{\pi,q}. \tag{5.41}$$

Thus this is indeed a near cancellation for time-even part in the velocity gauge O^+_{A-}. We note that this near cancellation is an inevitable result of the incompatibility of the time-reversal signatures of the two fundamental interactions H_E, H_{A1}. Without the closure approximation, the contributions of O^+_{A-} are weighted by a factor which vanishes in the closure limit and therefore is proportional to the photon frequency ω.



But this is precisely the factor which converts from that part of the vector potential **A** appropriate for photon annihilation to the appropriate part of its time derivative as in O^+_{E+}. Such conclusions are verified in a detailed calculation (Reid 1988). The gauge change may be implemented by the conversion from momentum to position operator, using

$$\mathbf{p} = \frac{im}{\hbar}[H_0, \mathbf{r}]. \tag{5.42}$$

The action of H_0 has the effect of introducing energy differences between the bra and ket state between which the position operator acts; and these nearly cancel, since in the two terms of eq. (5.38) these energy differences are of opposite sign. Reid (1988) recovers the standard Judd-Ofelt operator O^+_{E+} from O^+_{A-}.

We comment also that this reconciliation does not depend on variations in the eigenstates between gauges, a complication which Yang (1982) has explained in general and which Reid (1988) has suggested is relevant in this context. For, as Aharonov and Au (1979, 1981, 1982) show, the gauge change cannot affect an observable transition intensity at least in E1 coupling. Nor does it depend on the argument that if the eigenfunctions are chosen to be those of the energy operator ϵ, then the matrix elements obtained from H_{A1} and H_E are the same. This cannot hold in any case, since the time reversal selection rule gives very different results for these matrix elements in the closure limit. The wavefunctions in question are related by a unitary operator U, under which ϵ, since (in contrast to H_0) it is an observable, transforms as $U\epsilon U^\dagger$. This argument requires the relationship $UH_{A1}U^\dagger = H_E$ which does not hold. The E1

transition amplitudes formed from given eigenfunctions in any gauge are equivalent.

5.5 Second-order Coulomb interaction, two-body TRSRs, and Trees' correction

Now we discuss a two-body interaction term in second-order perturbation, the second-order Coulomb interaction and derive its corresponding TRSRs.

The (first-order) Coulomb interaction $\hat{H}_C = \frac{1}{2}\sum_{i\neq j} e^2/r_{ij}$ within a configuration is a time-even two-body operator. Slater's theory (Slater 1929) parameterized the Coulomb interaction with Slater parameters F_k. It can be written in tensorial form as

$$\hat{H}_C = \sum_{i\neq j,k} F_k[C_i^{(k)}C_j^{(k)}]^{(0)} \tag{5.43}$$

with even k and the tensor products are scalar in SO_3.

Similarly the orbit-orbit interaction is a time-even two-body physical operator

$$\hat{H}_{or} = \frac{-e^2}{2mc}[\frac{\mathbf{p}_i\mathbf{p}_j}{r_{ij}} + \frac{\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\mathbf{p}_i)\mathbf{p}_j}{r_{ij}^3}]$$

(Bethe and Salpeter 1957), which can be written in the tensorial form (Yanagawa 1955) as

$$\hat{H}_{or} = \sum_{i\neq j,k} M_k[C_i^{(k)}C_j^{(k)}]^{(0)} \tag{5.44}$$

with k odd (see also Wybourne 1970).

Trees (1951) first noted that "*adding a correction proportional to $L(L+1)$ to Slater's formulas greatly improved the accuracy of the theory in even configurations of first long period spectra.*" He later (Trees 1952) said "*no satisfactory simple theory to explain this effect has as yet been found.*" Racah (1952) pointed out that such correction terms in the d-shell $\alpha\phi_1(\mathbf{L}) + \beta\phi_2(\mathbf{L})$ where ϕ_1 and ϕ_2 are any functions of $\mathbf{L}$ can be written as $\sum_{i\neq j}[2\alpha\mathbf{l}_i\cdot\mathbf{l}_j + \beta q_{ij}]$ where q is a seniority operator. Trees and Jorgensen (1961) further discussed the physical origin of the Trees corrections and they pointed out "*Racah recognized that the correction implied a linear behaviour of second-order effects of the electrostatic (Coulomb) interaction. $\cdots$ Later it was recognized that the linear property of second-order perturbations has been demonstrated earlier by Bacher and Goudsmit (1934).*" It was then suggested that the "linear" second order

Coulomb interaction $\hat{H}_C^{(2)}$ can also be written in tensorial form as

$$\hat{H}_C^{(2)} = \sum_{i \neq j, t} B_t [U_i^{(t)} U_j^{(t)}]^{(0)} \tag{5.45}$$

with t odd, where $U_i^{(t)}$ is an effective one-body operator acting on particle i. Rajnak and Wybourne (1963) formulated Trees' three correction terms in the f-shell as $\alpha L(L+1) + \beta G(G_2) + \gamma G(R_7)$ where $G(G_2)$ and $G(R_7)$ are the eigenvalues of Casimir's operators for the groups G_2 and SO_7 respectively. They also proved that the tensor operators $U_i^{(t)} U_j^{(t)}$ with $t = 1, 3, 5$ are the linear combination of Casimir's operators of SO_3, G_2, and SO_7. Following this Racah and Stein (1967) gave a simpler formalism. Both Rajnak and Wybourne (1963) and Racah and Stein (1967) applied a strong closure approximation, the same as eq. (5.10), in their discussion as an *a priori* condition, where i is an intermediate configuration. Morrison and Rajnak (1971) gave a quantitative calculation of the second-order Coulomb interaction for the Trees parameters α, β, and γ of Pr^{3+} for each possible intermediate configuration apparently without the use of a strong closure approximation. It has also been generally accepted that although the orbit-orbit interaction has the same tensorial form as the linear second order Coulomb interaction, the contribution from the former is much smaller than the latter (Wybourne 1964).

Now we discuss the TRSRs appropriate for the second-order Coulomb interaction. The TRSR of Wang and Stedman (1992a,b) assumed that the operator under investigation is hermitian or anti-hermitian. For a product operator consisting of two operators to be hermitian, the two operators must commute. This holds when the operators are orbital and spin operator respectively, or when they are associated with different particles. The second-order Coulomb interaction belongs to this case, provided the form of the closure approximation used is as strong as that of eq. (5.10). In this case, according to the two-body TRSR (the first rule of Wang and Stedman (1992a), see eq. 3.29 in chapter 3) $t + t$ must be even, and according to especially eq. (4.26) and the discussion given in section 4.5.2 in chapter 4, each effective one-body component in eq. (5.45) must also obey the one-body TRSR, i.e. the rank t can only be *even* since the component operator is time-even. Hence the second-order Coulomb interaction cannot contribute to any Trees parameters under a strong closure approximation. The extent, then, of the contribution of second-order Coulomb interaction to any Trees terms is dictated by the extent to which the closure approximation of eq. (5.10) breaks down. We give a more detailed account below.

The matrix element of a second-order Coulomb interaction acting within the two-particle states l^2 can be written as $M = \sum_i \frac{1}{\Delta}\langle l^2|\frac{1}{r_{12}}|i\rangle\langle i|\frac{1}{r'_{12}}|l^2\rangle$ (let $e = 1$; i is the intermediate configuration). In tensorial form we have

$$M = \langle l^2|\sum_{k,q}\frac{r_<^k}{r_>^{k+1}}C_q^{(k)}(1)C_{-q}^{(k)}(2)\sum_i\frac{1}{\Delta}|i\rangle\langle i|\sum_{k',q'}\frac{r_<^{k'}}{r_>^{k'+1}}C_{q'}^{(k')}(1)C_{-q'}^{(k')}(2)|l^2\rangle, \qquad (5.46)$$

where the ranks k and k' are necessarily odd (even) if l^2 and i have the opposite (same) parity. The effective operator I ($M = \langle l^2|\ I\ |l^2\rangle$) within the coupled two-particle states $|l^2\rangle$ can be written, if the closure approximation eq. (5.10) is applied, as

$$I = \frac{1}{r_{12}r'_{12}\Delta} = \frac{1}{\Delta}\sum_{k,q}\frac{r_<^k}{r_>^{k+1}}C_q^{(k)}(1)C_{-q}^{(k)}(2)\sum_{k',q'}\frac{r_<^{k'}}{r_>^{k'+1}}C_{q'}^{(k')}(1)C_{-q'}^{(k')}(2). \qquad (5.47)$$

If we move operators for the same particle together, we obtain

$$I = \sum_{kqk'q'}\frac{r_<^{k+k'}}{r_>^{k+k'+2}}\frac{1}{\Delta}(C_q^{(k)}(1)C_{q'}^{(k')}(1))\ (C_{-q}^{(k)}(2)C_{-q'}^{(k')}(2)) = \sum_{t,r}B_tU_r^{(t)}(1)\ U_{-r}^{(t)}(2) \qquad (5.48)$$

where

$$U_r^{(t)}(1) \equiv \sum_{q,q'}\begin{pmatrix} t \\ -r \end{pmatrix}\begin{pmatrix} k & k' & t \\ q & q' & -r \end{pmatrix}C_q^{(k)}(1)C_{q'}^{(k')}(1),$$

$$U_{-r}^{(t)}(2) \equiv \sum_{q,q'}\begin{pmatrix} t \\ r \end{pmatrix}\begin{pmatrix} k & k' & t \\ -q & -q' & r \end{pmatrix}C_{-q}^{(k)}(2)C_{-q'}^{(k')}(2).$$

The operators acting on the same particle in eq. (5.47) commute,

$$[C_q^{(k)}(1), C_{q'}^{(k')}(1)] = 0, \quad [C_{-q}^{(k)}(2), C_{-q'}^{(k')}(2)] = 0. \qquad (5.49)$$

So, under the joint action HT, coupled effective one-body operators, $U_r^{(t)}(1)$ and $U_{-r}^{(t)}(2)$, must have the time reversal symmetry (HT phase) of their component operators and so must be HT-even. They are restricted by the one-body TRSR to have *even* rank (t) only. Therefore, under the closure approximation of eq. (5.10), each effective one-body component $U_i^{(t)}$ must obey a TRSR, and the second-order Coulomb interaction is ruled out as a possible contributor to the Trees terms.

However, since this strong closure approximation must run over all possible intermediate configurations including the ground configuration, and supposes that they all have the same energy separation, such an approximation cannot be good. Avoiding this approximation, one should calculate the effect of the second-order Coulomb

interaction for each possible intermediate configuration separately. The contribution of such a second-order Coulomb interaction within the ground configuration, i.e. the ground configuration to be the intermediate states as well as the initial and final states, might be expected to give the major contribution to Trees terms since its energy separation is the smallest. However, the perturbation formalism used by Lindgren and Morrison (1988) has the form of $PVQVP$ for second-order perturbation which forbids the ground configuration to be intermediate states due to the projection operator Q. Within a particular configuration only, the intermediate states are not complete. We can write the operator I' in the uncoupled basis as

$$\begin{aligned} I' = \sum_{kqk'q'} \frac{r_<^{k+k'}}{r_>^{k+k'+2}} \;\; & \frac{1}{\Delta} \;\; (C_q^{(k)}(1) \sum_{m_{l_1'}} |l_1'\rangle\langle l_1'|C_{q'}^{(k')}(1)) \; (C_{-q}^{(k)}(2) \sum_{m_{l_2'}} |l_2'\rangle\langle l_2'|C_{-q'}^{(k')}(2)) \\ & = \sum_{t,\rho} B_t' V_r^{(t)}(1) \; V_{-r}^{(t)}(2), \end{aligned} \tag{5.50}$$

where

$$\begin{aligned} V_r^{(t)}(1) \;\; &\equiv \;\; \sum_{q,q'} \begin{pmatrix} t \\ -r \end{pmatrix} \begin{pmatrix} k & k' & t \\ q & q' & -r \end{pmatrix} C_q^{(k)}(1) \sum_{m_{l_1'}} |l_1'\rangle\langle l_1'|C_{q'}^{(k')}(1), \\ V_{-r}^{(t)}(2) \;\; &\equiv \;\; \sum_{q,q'} \begin{pmatrix} t \\ r \end{pmatrix} \begin{pmatrix} k & k' & t \\ -q & -q' & r \end{pmatrix} C_{-q}^{(k)}(2) \sum_{m_{l_2'}} |l_2'\rangle\langle l_2'|C_{-q'}^{(k')}(2). \end{aligned}$$

Since, in this case, $C_q^{(k)}(1)$ and $C_{q'}^{(k')}(1)$ ($C_{-q}^{(k)}(2)$ and $C_{-q'}^{(k')}(2)$) do not commute, $V_r^{(t)}(1)$ and $V_{-\rho}^{(t)}(2)$ do not have a specific HT signature. In other words, they are not hermitian. Hence the TRSR is not applicable to the effective operator $V^{(t)}(i)$, and the rank t can be either even or odd.

To see this more clearly, we may take one more step, splitting eq. (5.50) further as in the following (we omit the intermediate states and the radial function in the expression for simplicity):

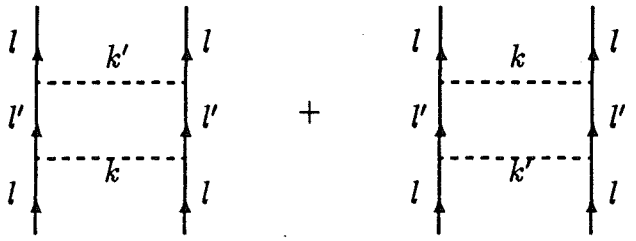
$$\begin{aligned} I \sim \frac{1}{4} \sum_{kqk'q'} \; \{ \;\; & [C_q^k C_{q'}^{k'}(1) + C_{q'}^{k'} C_q^k(1)] \; [C_{-q}^k C_{-q'}^{k'}(2) + C_{-q'}^{k'} C_{-q}^k(2)] \\ + \;\; & [C_q^k C_{q'}^{k'}(1) - C_{q'}^{k'} C_q^k(1)] \; [C_{-q}^k C_{-q'}^{k'}(2) - C_{-q'}^{k'} C_{-q}^k(2)] \\ + \;\; & [C_q^k C_{q'}^{k'}(1) - C_{q'}^{k'} C_q^k(1)] \; [C_{-q}^k C_{-q'}^{k'}(2) + C_{-q'}^{k'} C_{-q}^k(2)] \\ + \;\; & [C_q^k C_{q'}^{k'}(1) + C_{q'}^{k'} C_q^k(1)] \; [C_{-q}^k C_{-q'}^{k'}(2) - C_{-q'}^{k'} C_{-q}^k(2)] \; \}. \end{aligned} \tag{5.51}$$

Now since $[C^k C^{k'}(i) + C^{k'} C^k(i)]$ ($[C^k C^{k'}(i) - C^{k'} C^k(i)]$) is a symmetrised or hermitian (antisymmetrised or anti-hermitian) operator, under HT its HT signature is even (odd

respectively). Hence the operator having the form $[C^k C^{k'}(i) + C^{k'} C^k(i)]$ ($[C^k C^{k'}(i) - C^{k'} C^k(i)]$) is restricted by the one-body TRSR to have *even* (*odd*) coupled orbital ranks t only. Such a coupled tensor operator will be written as $T_i^{(+)}$ ($T_i^{(-)}$) where the superscript + (−) means even (odd) ranks and HT-even (HT-odd respectively). Thus the above equation can be rewritten in the form of coupled tensor operators as

$$I \sim \frac{1}{4}[T_i^{(+)} T_j^{(+)} + T_i^{(-)} T_j^{(-)} + T_i^{(-)} T_j^{(+)} + T_i^{(+)} T_j^{(-)}]. \tag{5.52}$$

The first and the second term correspond to the HT-even two-body interactions. The former has the same tensorial structure as the first-order Coulomb interaction and can be treated as the second-order corrections; the latter has the same tensorial form as the Trees correction terms, and they should also incorporate the effect of the orbit-orbit interaction. The last two terms are HT-odd. However if we sum over $kk'qq'$ these two terms cancel between themselves. To visualise this, we can draw the Goldstone diagrams for such a second-order Coulomb interaction as



One can apply the same approach as eq. (5.51) for these two diagrams, and two overall HT-odd two-body terms will be cancelled between these two diagrams. In other words, these two diagrams together represent a hermitian and HT-even two-body interaction. We can also see that under a strong closure approximation the HT-odd terms $[C^k C^{k'}(i) - C^{k'} C^k(i)]$ will reduce to zero and leave us with only $T_i^{(+)} T_j^{(+)}$ term. Hence each intermediate configuration can contribute to the Trees parameters, as shown by Morrison and Rajnak (1971) in their detailed calculations.

CHAPTER 6

Matter-field Interactions, Gauge Transformation, and Spin-forbidden Transitions

In chapter 2 we discussed the many-body perturbation theory appropriate for optical transition processes in general by using the Goldstone diagram method and associated Jucys-type angular momentum diagrams. For lanthanide ions in crystals or solutions, the intraconfigurational transitions are initially interpreted by the original Judd-Ofelt theory. It corresponds to one of the second-order Goldstone diagrams obtained in chapter 2. Selection rules on the ranks of the effective tensor operators obtained by Judd and Ofelt were reviewed in detail in chapter 5. The TRSR is helpful both here and in analysing the effect of a gauge transformation in Judd-Ofelt theory.

However, there are still some important questions concerned with optical transition theory to be answered. In E1 approximation the matter-field interaction is usually taken as $H_E \equiv -e\mathbf{E}\cdot\mathbf{r}$ in the length gauge and $H_A \equiv -e\mathbf{A}\cdot\mathbf{p}/m + e^2\mathbf{A}^2/2m$ in the velocity gauge although there is also a long controversy about their compatibility. The inadequacy of these two matter-field interactions in either gauge is evident when nominally spin-forbidden transitions are considered. Since these two operators are spin-independent, they cannot induce a truly spin-forbidden transition. In practice, the nominal spin-forbidden transitions are widely observed in atomic, molecular, and lanthanide ions in crystals and solutions, especially within the heavier elements. This is normally attributed to the fact that the nominal state is not strictly a pure single state in LS-coupling limit, but a mixture. This is rather true for heavier atoms.

The spin-orbit interaction $V_{SO} = \zeta\mathbf{s}\cdot\mathbf{l}$ is used to couple the total orbit angular momentum $\mathbf{L}$ and the total spin angular momentum $\mathbf{S}$ to the total angular momentum $\mathbf{J}$. Such inclusion of V_{SO} splits degenerate ^{2S+1}L state into $^{2S+1}L_J$ states and is called LS-coupling limit. In this limit the spin-orbit interaction is much weaker than the

Coulomb interaction and cannot couple different spin-states. Thus in this limit the spin-forbidden transitions $\Delta S \neq 0$ are strictly prohibited, although the spin-orbit interaction has been included in the unperturbed Hamiltonian. This is the case for the light elements. However, when the spin-orbit interaction becomes stronger, the LS-coupling limit is no longer a good approximation. In another extreme, the spin-orbit interaction is larger than Coulomb interaction and leads to jj-coupling where the total spin **S** and total angular momentum **L** are no longer the good quantum numbers, and the spin-forbidden transitions $\Delta S \neq 0$ are meaningless in this limit. In between, the "intermediate coupling" approximation uses the LS-coupling states as the bases, and the spin-orbit interaction is also strong enough to mix states with different total spin **S** into the true energy eigenfunctions. This *intermediate coupling* means that different S-states with the same J can be mixed up since the spin-orbit interaction is a scalar in J-manifold (SO_3^J). This is the case for heavier elements and is the normal explanation for the nominal "spin-forbidden" transitions with spin-independent matter-field interaction in these atoms. As early as 1968, Wybourne suggested that this spin-orbit interaction can be further included within the effective transition operator in a third-order perturbation for lanthanide intra-configurational transitions, and such an effective transition operator becomes "spin-dependent". This can be justified according to our diagram perturbation analysis discussed in chapter 2. The spin-orbit interaction V_{SO} appears in the first-order diagram (diagram (a) of Fig. 2.5) and the third-order diagrams (diagrams (b) and (c) in Fig. 2.9). The former serves as an energy modification and the latter as an effective transition operator. Judd and Pooler (1982), Downer *et al.* (1988), and Burdick *et al.* (1989) gave the further developments along this line.

For light atoms such as helium, the spin-orbit interaction is very weak, and the LS-coupling is a very good approximation. The spin-forbidden transition between spin-singlets (para-helium) and the spin-triplets (ortho-helium) is prohibited. However, such spin-forbidden transitions in helium are observed as strong features of the spectra of high-temperature plasma and the solar corona (Drake and Dalgarno 1969). The relativistic spin-dependent corrections for the electron wavefunction were considered to give the explanation (Drake 1971, 1972, 1976).

The spin-orbit interaction and also spin-spin, spin-other-orbit, and orbit-orbit interactions come from relativistic corrections in Dirac theory. We may ask whether there are also some similar relativistic spin-corrections for matter-field interaction

even in the E1 limit at the first place. Bjorken and Drell (1964), Trigg (1964), and Brink and Satchler (1968), Drake (1971, 1972), and Sebastian (1981, 1982) start with the Dirac equation and use the Foldy-Wouthuysen (FW) transformation to obtain the relativistic corrections for non-relativistic Schrödinger particles. Drake (1971) obtained a new spin-dependent matter-field interaction $H_T = -e\zeta \mathbf{A} \cdot \mathbf{s} \times \mathbf{r}$ in the velocity gauge, and pointed out that it is cancelled out in the length gauge. Sebastian obtained another spin-dependent matter-field interaction and used it for the charmonium system, concluding that the matter-field interaction is spin-independent in E1 limit.

In section 6.1 we carry out again this FW transformation of the Dirac equation for the simplest case, a single electron. We reanalyse the relativistic corrections to the Schrödinger equation and find in the E1 limit another spin-dependent matter-field interaction $H'_S = e\dot{\mathbf{A}} \cdot \mathbf{s} \times \mathbf{p}/2m^2c^2$ in both gauges, which is of potential relevance to Judd-Ofelt theory for intra-configurational transitions (see section 6.3.1) and also to the first-order transition operator for inter-configurational transitions (see section 6.3.2). In section 6.2 the gauge transformation conventionally used to convert H_{A1} to H_E is applied to the whole system Hamiltonian including all spin-dependent relativistic correction terms. We confirm the conclusion of Drake (1972, 1976) that H_T is cancelled out exactly in the length gauge. We also find that H'_S is the same in both gauges in E1 limit. The gauge transformation property of the M1 operators which although is not our main interest can also be analysed. It turns out that the compatibility of the matter-field interaction operators in two different gauges is much more complicated when spin is included. A related problem associated with the second-quantised formalism for radiation field is also discussed in section 6.2. In section 6.3 the practical applications of this new E1 spin-dependent operator H'_S are discussed for interconfigurational and intraconfigurational transitions. The TRSRs are also used to restrict the possible spin-orbital ranks of the effective tensor operators and to define the different roles of the different operators.

6.1 Matter-field interaction, Foldy-Wouthuysen transformation and Dirac equation

We will restrict ourselves to the simplest case of a one-particle system only in this section. In quantum mechanics, the interaction between the electron and electromagnetic

field is introduced by *minimal coupling*, i.e. by replacing the canonical momentum $\mathbf{p}$ of the electron with the *kinetic momentum* $\boldsymbol{\pi} \equiv \mathbf{p} - e\mathbf{A}$. In nonrelativistic quantum mechanics, minimal coupling immediately leads to the result that the system (of the electron plus the electromagnetic field) Hamiltonian can be written as

$$H = \frac{(\mathbf{p} - e\mathbf{A})^2}{2m} + e\Phi + \frac{1}{8\pi}\int d^3x(E^2 + B^2) = H_0 + H_I + H_{rad}, \tag{6.1}$$

where the scalar potential Φ is the superposition of the Coulomb potential of the nucleus Φ_C and the radiation field Φ_{rad}, i.e. $\Phi = \Phi_C + \Phi_{rad}$. For the radiation field we may choose the Coulomb gauge with $\nabla \cdot \mathbf{A} = 0$, and $\Phi_{rad} = 0$. We thus have $H_0 = p^2/2m + e\Phi_C$, $H_{rad} = \frac{1}{8\pi}\int d^3x(E^2 + B^2)$, and $H_A^I = -\frac{e}{m}\mathbf{A}\cdot\mathbf{p} + \frac{e^2}{2m}A^2$. In the following the superscript I referring to the interaction Hamiltonian will be omitted. The linear part of the matter-field interaction within this *velocity gauge* is then

$$H_{A1} = -\frac{e}{m}\mathbf{A}\cdot\mathbf{p}. \tag{6.2}$$

This form of the interaction, on expansion in multipoles, can be used to calculate the strengths of the various optical transition processes.

At the more fundamental level of relativistic quantum mechanics, Dirac particles in an external electromagnetic field are described by the minimally coupled Dirac Hamiltonian,

$$H_D = c\boldsymbol{\alpha}\cdot\boldsymbol{\pi} + \beta mc^2 + e\Phi_C, \tag{6.3}$$

where $\boldsymbol{\alpha}$ and β are the Dirac 4×4 matrices. The 4 components of the Dirac equation describe the electron and positron. Again, when the Coulomb gauge is chosen for the external field as indicated in the above equation, the relativistic interaction Hamiltonian is

$$H_D^I = -ce\boldsymbol{\alpha}\cdot\mathbf{A}. \tag{6.4}$$

$\boldsymbol{\alpha}$ anti-commutes with the Dirac matrix β; such an operator is called *odd*. The Dirac equation can then be decomposed into two two-component equations, and the electron equation reduces to a Pauli-like description in the non-relativistic limit. The associated modifications to the non-relativistic Schrödinger equation are relativistic corrections; most of them are spin-dependent. The non-relativistic Schrödinger-Pauli Hamiltonian is adequate to describe the electron with spin only when judiciously interpreted (see e.g. Gurtler and Hestenes (1975)). We know from Trigg (1964), Bjorken and Drell (1964), and Brink and Satchler (1968) that the matter-field interaction H_A

is insufficient when spin is included. In this section we will discuss primarily the possible spin-dependent corrections for the matter-field interaction H_A in the velocity gauge. In the next section, a gauge transformation to the length gauge will be discussed.

Following Bjorken and Drell (1964) and Trigg (1964), the Dirac Hamiltonian is written as

$$H_D = \beta mc^2 + \mathcal{E} + \mathcal{O} \tag{6.5}$$

with the odd operator $\mathcal{O}$ initially being $c\boldsymbol{\alpha}\cdot(\mathbf{p}-e\mathbf{A})$, and the even operator $\mathcal{E} = e\Phi_C$. Under a unitary transformation $U = e^{iS}$, the Dirac equation $H_D\psi = \mathrm{i}\hbar\frac{\partial}{\partial t}\psi$ becomes

$$[UH_DU^\dagger + \mathrm{i}\hbar\dot{U}U^\dagger]\psi' = \mathrm{i}\hbar\frac{\partial}{\partial t}\psi', \tag{6.6}$$

where $\psi' = U\psi$, so that we have $H'_D = UH_DU^\dagger + \mathrm{i}\hbar\dot{U}U^\dagger$. Under a Baker-Campbell-Hausdorff expansion up to the required accuracy of $O(\mu^2)$ we have

$$\begin{aligned} H'_D = H_D + \mathrm{i}[S, H_D] + \frac{\mathrm{i}^2}{2}[S,[S,H_D]] - \frac{\mathrm{i}}{6}[S,[S,[S,H_D]]] \\ + \frac{1}{24}[S,[S,[S,[S,H_D]]]] - \hbar\dot{S} - \frac{\mathrm{i}\hbar}{2}[S,\dot{S}]. \end{aligned} \tag{6.7}$$

Taking $S = -\mathrm{i}\beta\mathcal{O}/2mc^2$ we obtain

$$H'_D = \beta m + \mathcal{E}' + \mathcal{O}', \tag{6.8}$$

where

$$\begin{aligned} \mathcal{E}' &= \beta\left(\frac{\mathcal{O}^2}{2mc^2} - \frac{\mathcal{O}^4}{8m^3c^6}\right) + \mathcal{E} - \frac{1}{8m^2c^4}[\mathcal{O},[\mathcal{O},\mathcal{E}]] - \frac{\mathrm{i}}{8m^2c^4}[\mathcal{O},\dot{\mathcal{O}}] \\ \mathcal{O}' &= \frac{\beta}{2m^2}[\mathcal{O},\mathcal{E}] - \frac{\mathcal{O}^3}{3m^2c^4} + \frac{\mathrm{i}\beta\dot{\mathcal{O}}}{2mc^2} \end{aligned}$$

Since even (odd) products of the odd operator $\mathcal{O}$ are even (odd), $\mathcal{E}'$ is an even operator and $\mathcal{O}'$ is odd operator. Under another two successive unitary Foldy-Wouthuysen (FW) transformations, all of the odd operators after the first FW transformation can be transformed away to order $\mathrm{O}(c^{-2})$. These two FW transformations are $U' = e^{\mathrm{i}S'}$, and $U'' = e^{\mathrm{i}S''}$ with

$$\begin{aligned} S' &= -\frac{\mathrm{i}\beta\mathcal{O}'}{2mc^2} \\ S'' &= -\frac{\mathrm{i}\beta\mathcal{O}''}{2mc^2} = -\frac{\mathrm{i}\beta}{2mc^2}\left(\frac{\beta}{2mc^2}[\mathcal{O}',\mathcal{E}'] + \frac{\mathrm{i}\beta\dot{\mathcal{O}}'}{2mc^2}\right). \end{aligned}$$

The Dirac Hamiltonian then becomes to $O(c^{-2})$ (see Bjorken and Drell (1964) p51)

$$\begin{aligned} H_D''' &= \beta mc^2 + \mathcal{E}' \\ &= \beta(mc^2 + \frac{\mathcal{O}^2}{2mc^2} - \frac{\mathcal{O}^4}{8m^3c^6}) + \mathcal{E} - \frac{1}{8m^2c^4}[\mathcal{O},[\mathcal{O},\mathcal{E}]] - \frac{\mathrm{i}}{8m^2c^4}[\mathcal{O},\dot{\mathcal{O}}] \quad (6.9) \end{aligned}$$

plus higher order terms. All operators in H_D''' are even operators, which is just the objective of such FW transformations.

By carrying out the calculation for eq. (6.9), we finally obtain

$$\begin{aligned} H_D''' &= \beta mc^2 + e\Phi_C + \frac{\beta}{2m}(\mathbf{p} - e\mathbf{A})^2 - \frac{e\hbar}{2m}\beta\boldsymbol{\sigma}\cdot\mathbf{B} - \frac{e\hbar^2}{8m^2c^2}\nabla\cdot\mathbf{E} \\ &\quad -\frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot[\mathbf{E}\times(\mathbf{p} - e\mathbf{A}) + \frac{\mathrm{i}\hbar}{2}\nabla\times\mathbf{E}]. \quad (6.10) \end{aligned}$$

Trigg (1964) basically obtained this result in his eq. (11.232-27) except for a sign difference in the last term of eq. (6.10). Equation (4.5) of Bjorken and Drell (1964) has a similar result but $-e\mathbf{A}$ in the last term of eq. (6.10) is omitted because they linearize in the field; this approximation is inadequate. Comparing with eq. (6.1) we find the relativistic corrections.

Normally, in standard text books such as Bethe and Salpeter (1957), Trigg (1964), Bjorken and Drell (1964), the interpretations of these corrections are restricted to a discussion of the electron energy corrections. For example, the last term is explained as the spin-orbit interaction V_{SO}. The latter indeed comes from eq. (6.10) if the electric field $\mathbf{E}$ is taken as the spherical Coulomb field $\mathbf{E}_C$ of the nucleus;

$$\mathbf{E}_C = -\frac{\mathbf{r}}{r}\frac{\partial(\Phi_C)}{\partial r} = -\frac{Ze}{4\pi\epsilon_0 r^3}\mathbf{r}, \qquad \nabla\times\mathbf{E}_C = 0. \quad (6.11)$$

The term $-\frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot\mathbf{E}_C\times\mathbf{p}$ within eq. (6.10) indeed leads to

$$V_{SO} \equiv -\frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(-\frac{Ze}{4\pi\epsilon_0 r^3}\mathbf{r})\times\mathbf{p} = \zeta\mathbf{s}\cdot\mathbf{l}, \quad (6.12)$$

where $\zeta = Ze^2/8\pi\epsilon_0 m^2c^2r^3$ and $\mathbf{s} = \hbar\boldsymbol{\sigma}/2$.

However the last term of eq. (6.10) even with the Coulomb electric field $\mathbf{E}_C$ also contains

$$H_T \equiv -\frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(-\frac{Ze}{4\pi\epsilon_0 r^3}\mathbf{r})\times(-e\mathbf{A}) = -e\zeta\mathbf{A}\cdot\mathbf{s}\times\mathbf{r}. \quad (6.13)$$

This operator is a spin-dependent *matter-field interaction* operator. It should be taken as one of the spin-dependent corrections for H_A in eq. (6.1). Drake explicitly (1971,1972) presented this operator as a spin-dependent matter-field interaction.

Second, the total electric field $\mathbf{E}$ is

$$\mathbf{E} = -\nabla\Phi_C - \frac{\partial \mathbf{A}}{\partial t} = \mathbf{E}_C + \mathbf{E}_{rad}. \tag{6.14}$$

Therefore a complete expression for the last term of eq. (6.10) is

$$-\frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot[(\mathbf{E}_C + \mathbf{E}_{rad}) \times (\mathbf{p} - e\mathbf{A}) + \frac{i\hbar}{2}\nabla \times \mathbf{E}_{rad}] = V_{SO} + H_T + H_S. \tag{6.15}$$

Thus another spin-dependent matter-field interaction operator H_S is obtained,

$$\begin{aligned} H_S &\equiv -\frac{e}{2m^2c^2}\mathbf{s}\cdot(\mathbf{E}_{rad} \times \mathbf{p} + \frac{i\hbar}{2}\nabla \times \mathbf{E}_{rad}) \\ &= \frac{e}{4m^2c^2}\mathbf{s}\cdot(\mathbf{p} \times \mathbf{E}_{rad} - \mathbf{E}_{rad} \times \mathbf{p}) \\ &= \chi[(\mathbf{s} \times \mathbf{p})\cdot\mathbf{E}_{rad} - \mathbf{E}_{rad}\cdot(\mathbf{s} \times \mathbf{p})] \end{aligned} \tag{6.16}$$

where $\chi = e/4m^2c^2$. Sebastian (1979, 1981, 1982) first proposed this operator as part of the matter-field interaction operator and used it as a starting point to calculate one-photon transition rates in charmonium. It is noted that V_{SO} and H_T are associated with a Coulomb central field, but H_S is not. In the E1 approximation, H_S reduces to

$$H'_S \equiv -\frac{e}{2m^2c^2}\mathbf{E}_{rad}\cdot(\mathbf{s} \times \mathbf{p}). \tag{6.17}$$

We note that the interaction Hamiltonian used by Sebastian (1982), his eq. (1) in this paper, does not contain H_T and the spin-orbit interaction V_{SO} is not included in the Hamiltonian either, since he omits the central field. In Drake's expression for the interaction Hamiltonian, eq. (28) of Drake (1971), H_S is absent. We see no reason for this omission.

The fourth term of eq. (6.10), $-e\mathbf{s}\cdot\mathbf{B}/m$, can also be included as a spin-dependent matter-field interaction H_B, an expression which gives as well as the Zeeman coupling to a static field with $g_s = 2$, a further matter-field interaction as mentioned by Brink and Satchler (1968).

Hence, finally in the velocity gauge, we can write the total matter-field interaction with all relativistic spin-corrections to $O(c^{-2})$ as

$$\begin{aligned} H_I &= H_A + H_T + H_S + H_B \\ &= -\frac{e}{m}\mathbf{A}\cdot\mathbf{p} + \frac{e^2}{2m}A^2 - e\zeta\mathbf{A}\cdot(\mathbf{s} \times \mathbf{r}) \\ &\quad +\chi[(\mathbf{s} \times \mathbf{p})\cdot\mathbf{E}_{rad} - \mathbf{E}_{rad}\cdot(\mathbf{s} \times \mathbf{p})] - \frac{e}{m}\mathbf{s}\cdot\mathbf{B}. \end{aligned} \tag{6.18}$$

Let us write the relativistic mass increase term and the Darwin term together as $H_R = \beta mc^2 - \frac{e\hbar^2}{8m^2c^2}\nabla \cdot \mathbf{E}$. Thus the system Schrödinger Hamiltonian eq. (6.1) can be modified with all relativistic spin-corrections, in the velocity gauge, to $O(c^2)$ as

$$\begin{aligned} H_{rc} &= e\Phi_C + \frac{1}{2m}[\boldsymbol{\pi}^2 - 2e\mathbf{s}\cdot\mathbf{B}] + \frac{e}{4m^2c^2}\mathbf{s}\cdot[\boldsymbol{\pi}\times\mathbf{E} - \mathbf{E}\times\boldsymbol{\pi}] + H_R + H_{rad} \\ &= e\Phi_C + \frac{\mathbf{p}^2}{2m} + H_A + H_B + V_{SO} + H_T + H_S + H_R + H_{rad}. \end{aligned} \tag{6.19}$$

6.2 Gauge transformation

Let us for the moment revert to a non-relativistic Schrödinger Hamiltonian, eq. (6.1).

The gauge invariance of quantum theory implies that either $H_{A1} = -e\mathbf{A}\cdot\mathbf{p}/m$ (in the velocity gauge) or $H_E = -e\mathbf{E}_{rad}\cdot\mathbf{r}$ (in the length gauge) for the matter-field interaction Hamiltonian may be used for calculations in atomic physics. The best choice of operator has been discussed from the earliest days of quantum theory (various origins are traced in Kobe (1979), Forney *et al.* (1977) and Zukowski (1985)). Grant (1974) and Grant and Starace (1975) discuss the relativistic case. The derivative form of the operator $\mathbf{p}$ makes calculations with H_A difficult; intermediate states of higher energy and indeed the continuum contribute more strongly in this choice. For such reasons H_E is usually favoured in practical calculations.

Many authors support the use of H_E (e.g. Lamb *et al.* (1987), Yang (1976, 1982), Kobe and Golshan (1987), Forney *et al.* 1977, Zukowski 1985, Leone *et al.* (1985), Leubner and Zoller (1980), Leubner (1981a, 1981b)), while others (Aharonov and Au (1979,1981, 1983), Feutchwang *et al.* (1984)) defend the use of H_A for calculation of observable quantities. One issue at stake is whether H_E is unique in permitting direct calculation of gauge-invariant and so observable quantities. Another is the choice of independent variables in ensuring Maxwell's equations (Haller (1982), Healy (1982), Power and Thirunamachandran (1982a, 1982b) for example). Aharonov and Au (1981, 1982) in their defences of the use of H_A have argued that neither the difference in unperturbed wavefunction nor the apparent gauge variance of matrix elements of H_A disqualifies their applicability for an analysis of experiment.

The replacement of H_A by H_E may be accomplished by a gauge transformation of the classical radiation fields: $\mathbf{A} \rightarrow \mathbf{A}+\nabla\chi$, $\Phi_{rad} \rightarrow \Phi_{rad}-\partial\chi/\partial t$. In E1 approximation (when $\mathbf{A}$ is not space dependent) the choice $\chi \equiv -\mathbf{A}\cdot\mathbf{r}$ takes us from a Hamiltonian in which only $\mathbf{A}$ is nonzero (velocity gauge) to one in which only Φ_{rad} is nonzero (length

gauge). This change may in turn be represented as a canonical unitary transformation of the Hamiltonian, whose generator is $U_g = e^{iS_g}$ with $S_g = e\chi/\hbar = -e\mathbf{A}\cdot\mathbf{r}/\hbar$. The unperturbed wavefunctions Ψ therefore differ by a unitary transformation $\Psi \rightarrow \Psi' = U_g\Psi$.

In the context of quantum field theory, the Dirac equation in the form of a minimal coupling with the A_μ field is *gauge invariant.* In a non-relativistic limit, under the unitary gauge transformation, the time-dependent Schrödinger equation is *gauge covariant,*

$$H\Psi = i\hbar\frac{\partial}{\partial t}\Psi \;\rightarrow\; [U_g H U_g^\dagger + i\hbar\dot{U}_g U_g^\dagger]\Psi' = i\hbar\frac{\partial}{\partial t}\Psi'. \tag{6.20}$$

In general, the Hamiltonian should include both electron and the radiation field.

Under such a gauge transformation, the classical radiation Hamiltonian H_{rad} is invariant, $U_g H_{rad} U_g^\dagger = H_{rad}$, since it depends only on the (gauge invariant) physical fields. Due to this fact, the radiation Hamiltonian H_{rad} may be omitted from the system Hamiltonian when the gauge transformation is discussed. We only need to discuss the electronic matrix elements.

However, this result does not hold for the second quantised radiation Hamiltonian $\hat{H}_{rad}$,

$$\hat{H}_{rad} = \sum_k \hbar\omega_k(a_k^\dagger a_k + \frac{1}{2}). \tag{6.21}$$

By using (Sakurai 1965) $\hat{\mathbf{A}}(\mathbf{r},t) = \sum_k c\omega_k^{\frac{1}{2}} a_k e_k \exp[-i(\omega_k t - \mathbf{k}\cdot\mathbf{r})] + h.c$ where $a_k^\dagger$ creates a photon in mode k with energy $\hbar\omega_k$, under the gauge transformation $\hat{U}_g \equiv e^{i\hat{S}_g}$ with $\hat{S}_g = -e\hat{\mathbf{A}}\cdot\mathbf{r}/\hbar$ we have

$$\hat{U}_g\hat{H}_{rad}\hat{U}_g^\dagger = \hat{H}_{rad} + [i\hat{S}_g, \hat{H}_{rad}] + \frac{1}{2!}[i\hat{S}_g, [i\hat{S}_g, \hat{H}_{rad}]] + \cdots. \tag{6.22}$$

Since $[(a + a^\dagger), a^\dagger a] = a - a^\dagger$ (see e.g. Aharonov and Au 1979), we have

$$[-\frac{ie}{\hbar}\hat{\mathbf{A}}\cdot\mathbf{r}, \sum_k \hbar\omega_k a_k^\dagger a_k] = -e\hat{\mathbf{E}}\cdot\mathbf{r}.$$

Therefore, by using the second quantised formalism one obtains an extra $\hat{H}_E$ from the gauge transformation of the radiation Hamiltonian $\hat{H}_{rad}$ in addition to another $\hat{H}_E$ arising from $i\hbar\dot{U}_g U_g^\dagger$ in eq. (6.20). This complication seems not to have been noted before. On the other hands, the second quantised transformation operator $\hat{U}_g$ dresses the electronic states with photons, leading to a very different structure of perturbation theory. For these reasons we will use a classical and not a second quantised vector potential in the following.

6.2.1 Length gauge form in E1 limit

Under the gauge transformation of eq. (6.20) the kinetic momentum $\boldsymbol{\pi}$ transforms as follow.

$$U_g \boldsymbol{\pi} U_g^\dagger = \mathbf{p} + e(\mathbf{r}\cdot\nabla)\mathbf{A} + e\mathbf{r}\times(\nabla\times\mathbf{A}) \equiv \mathbf{P}, \tag{6.23}$$

since we have

$$\begin{aligned} U_g \boldsymbol{\pi} U_g^\dagger &= \mathbf{p} - e\mathbf{A} + [-\mathrm{i}\frac{e}{\hbar}\mathbf{A}\cdot\mathbf{r}, \mathbf{p}], \\ \mathrm{i}\hbar\nabla(\mathbf{A}\cdot\mathbf{r}) &= \mathrm{i}\hbar[(\mathbf{A}\cdot\nabla)\mathbf{r} + (\mathbf{r}\cdot\nabla)\mathbf{A} + \mathbf{r}\times\nabla\times\mathbf{A}]. \end{aligned}$$

If (as in the E1 approximation) the spatial derivatives of $\mathbf{A}$ are ignored, we then obtain $U_g \boldsymbol{\pi} U_g^\dagger = \mathbf{p}$.

Hence, when the non-relativistic limit ($H = e\Phi_C + \boldsymbol{\pi}^2/2m + H_{rad}$, eq. 6.1) is taken, a classical radiation field is chosen for radiation, and the E1 limit is made, H_E and H_A transform into one another under the gauge transformation (eq. 6.20);

$$U_g(e\Phi_C + \frac{\boldsymbol{\pi}^2}{2m} + H_{rad})U_g^\dagger = e\Phi_C + \frac{\mathbf{p}^2}{2m} + H_{rad}; \quad \mathrm{i}\hbar\dot{U}_g U_g^\dagger = e\mathbf{r}\cdot\dot{\mathbf{A}} = H_E, \tag{6.24}$$

and thus, in the length gauge,

$$H' = e\Phi_C + \frac{\mathbf{p}^2}{2m} + e\mathbf{r}\cdot\dot{\mathbf{A}} + H_{rad}. \tag{6.25}$$

Therefore the compatibility of H_E and H_{A1} in the two gauges can be realised only under these extreme conditions mentioned above.

We now add to the electronic Hamiltonian all the relativistic spin-corrections, H_{rc} of eq. (6.19). Since we omit the spatial derivatives of $\mathbf{A}$ (in E1 limit) under the gauge transformation

$$\begin{aligned} U_g \boldsymbol{\pi}^2 U_g^\dagger &= \mathbf{p}^2, \\ U_g(\chi\mathbf{s}\cdot[\boldsymbol{\pi}\times\mathbf{E} - \mathbf{E}\times\boldsymbol{\pi}])U_g^\dagger &= \chi\mathbf{s}\cdot[\mathbf{p}\times\mathbf{E} - \mathbf{E}\times\mathbf{p}] = V_{SO} + H_S, \\ U_g(e\Phi_C + H_B + H_R + H_{rad})U_g^\dagger &= e\Phi_C + H_B + H_R + H_{rad}, \\ \mathrm{i}\hbar\dot{U}_g U_g^\dagger &= e\mathbf{r}\cdot\dot{\mathbf{A}} = H_E, \end{aligned}$$

and we have, in the length gauge to $\mathrm{O}(c^2)$,

$$\begin{aligned} H'_{rc} &= e\Phi_C + \frac{1}{2m}[\mathbf{p}^2 - 2e\mathbf{s}\cdot\mathbf{B}] + \frac{e}{4m^2c^2}\mathbf{s}\cdot[\mathbf{p}\times\mathbf{E} - \mathbf{E}\times\mathbf{p}] + e\mathbf{r}\cdot\dot{\mathbf{A}} + H_R + H_{rad} \\ &= H_0 + H_B + V_{SO} + H_S + H_E + H_R + H_{rad}. \end{aligned} \tag{6.26}$$

H_T cancels out exactly in the length gauge. This verifies the statements of Drake (1972, 1976), i.e. H_E in the length gauge is equivalent to $H_A + H_T$ in the velocity gauge. The reason for this cancellation is clarified in the above: the replacement of $\boldsymbol{\pi}$ by $\mathbf{p}$ which is the hallmark of the gauge transformation which simply eliminates H_T. This also indicates that when spin is involved H_A and H_E are no longer compatible. On the other hand, we will show in the next section that when higher orders of perturbation are considered, an operator similar to H_T may also appear in the length gauge. This has not been noticed before.

6.2.2 General length gauge form, E1 and M1 operators

Now we discuss a more general form of the gauge transformation of the system Hamiltonian from the velocity gauge (eq. 6.19) to the length gauge. In the last subsection, under the gauge transformation $U_g \boldsymbol{\pi} U_g^\dagger = \mathbf{p}$ is only an approximation which is in accord with the E1 limit. In general, we have

$$U_g \boldsymbol{\pi} U_g^\dagger = \mathbf{P} \equiv \mathbf{p} + e(\mathbf{r}\cdot\nabla)\mathbf{A} + e\mathbf{r}\times\mathbf{B}$$

(eq. 6.23), under this general gauge transformation one has

$$\begin{aligned} U_g \boldsymbol{\pi}^2 U_g^\dagger &= \mathbf{P}^2, \\ U_g(\chi \mathbf{s}\cdot[\boldsymbol{\pi}\times\mathbf{E} - \mathbf{E}\times\boldsymbol{\pi}])U_g^\dagger &= \chi \mathbf{s}\cdot[\mathbf{P}\times\mathbf{E} - \mathbf{E}\times\mathbf{P}], \\ U_g(e\Phi_C + H_B + H_R + H_{rad})U_g^\dagger &= e\Phi_C + H_B + H_R + H_{rad}, \\ i\hbar \dot{U}_g U_g^\dagger &= e\mathbf{r}\cdot\dot{\mathbf{A}} = H_E. \end{aligned}$$

Thus, in general, the system Hamiltonian H_{re} (eq. 6.19) transforms to the length gauge as

$$H''_{rc} = e\Phi_C + \frac{1}{2m}(\mathbf{P}^2 - 2e\mathbf{s}\cdot\mathbf{B}) + \frac{e}{4m^2c^2}\mathbf{s}\cdot(\mathbf{P}\times\mathbf{E} - \mathbf{E}\times\mathbf{P}) + e\mathbf{r}\cdot\dot{\mathbf{A}} + H_R + H_{rad}. \quad (6.27)$$

where $\mathbf{E} = \mathbf{E}_C + \mathbf{E}_{rad}$.

If we only keep the terms linearized in the electromagnetic field, the term $\frac{e}{4m^2c^2}\mathbf{s}\cdot(\mathbf{P}\times\mathbf{E} - \mathbf{E}\times\mathbf{P})$ reduces to $\frac{e}{4m^2c^2}\mathbf{s}\cdot(\mathbf{p}\times\mathbf{E} - \mathbf{E}\times\mathbf{p})$, and the second term in eq. (6.27) can be written as

$$\frac{1}{2m}\mathbf{P}^2 = \frac{1}{2m}(\mathbf{p} + e(\mathbf{r}\cdot\nabla)\mathbf{A} + e\mathbf{r}\times\mathbf{B})^2 \simeq \frac{\mathbf{p}^2}{2m} - \frac{e}{m}\mathbf{l}\cdot\mathbf{B} + \frac{ie}{m\hbar}(\mathbf{r}\cdot\mathbf{p})\mathbf{A}\cdot\mathbf{p} \quad (6.28)$$

where the last term comes from $[\mathbf{p}\cdot e(\mathbf{r}\cdot\nabla)\mathbf{A}+e(\mathbf{r}\cdot\nabla)\mathbf{A}\cdot\mathbf{p}]/2m$ and we still use the Coulomb gauge $\nabla\cdot\mathbf{A}=0$ for the radiation field. Hence the whole system Hamiltonian can be expressed in the length gauge as

$$H''_{rc}\simeq\Phi_C+\frac{\mathbf{p}^2}{2m}-\frac{e}{m}\mathbf{l}\cdot\mathbf{B}+\frac{ie}{m\hbar}(\mathbf{r}\cdot\mathbf{p})\mathbf{A}\cdot\mathbf{p}-\frac{e}{m}\mathbf{s}\cdot\mathbf{B}+\frac{e}{4m^2c^2}\mathbf{s}\cdot(\mathbf{p}\times\mathbf{E}-\mathbf{E}\times\mathbf{p})$$

$$+e\mathbf{r}\cdot\dot{\mathbf{A}}+H_R+H_{rad}=H_0+H_L+H_p+H_B+V_{SO}+H_S+H_E+H_R+H_{rad}. \quad (6.29)$$

Two new matter-field interactions which do not appear under the approximation $U_g\pi U_g^\dagger=\mathbf{p}$ are

$$H_L\equiv-2\mu_b\mathbf{l}\cdot\mathbf{B};\quad H_p\equiv\frac{ie}{m\hbar}(\mathbf{r}\cdot\mathbf{p})\mathbf{A}\cdot\mathbf{p}, \quad (6.30)$$

where $\mu_b=e/2m$ is the Bohr magneton. According to the parity classification of the electromagnetic field, H_L and H_d belong to M1 and E1 matter-field interaction operators respectively.

Thus we can write all possible linearised matter-field interactions in the length gauge as

$$H^I=(H_E+H'_S+H_p)\ +\ (H_L+H_B+H''_S) \quad (6.31)$$

where $(H_E+H'_S+H_p)$ are the E1 operators and $(H_L+H_B+H''_S)$ are M1 operators.

For M1 operators in the length gauge we have

$$H_L=-2\mu_b\mathbf{l}\cdot\mathbf{B};\quad H_B=-2\mu_b\mathbf{s}\cdot\mathbf{B};\quad H''_S=-\frac{ie\hbar}{4m^2c^2}\mathbf{s}\cdot\dot{\mathbf{B}}.$$

Both H_B and H''_S have been obtained in the velocity gauge, eq. (6.26), and are gauge-invariant. The H''_S operator is the M1 part of the operator H_S which only interact with time-varying magnetic field. The H_B and H_L operators describe the spin and orbital magnetic interaction respectively in general.

6.2.3 Spacetime symmetries of E1 and M1 matter-field interaction operators

Now we discuss the spacetime symmetries of these various interaction operators and the corresponding electronic selection rules for intra-configuration transitions, i.e. the parity selection rule (PSR) and time reversal selection rule (TRSR) (Wang and Stedman 1992a,b). The PSR requires that any electronic intra-configuration transition operator must be parity-even. The one-body TRSR requires that HT-even (HT-odd) electronic operator within a spin-orbital multiplet must have even (odd) spin-orbital ranks.

The system total Hamiltonian including various matter-field interactions either in the velocity gauge (eq. 6.19) or in the length gauge (eq. 6.29) including E1 and M1 operators is overall spatial reflection and time reversal invariant (parity-even and time-even). But the electronic operator in a matter-field interaction need not necessarily be parity-even and time-even. For example in H_E, the electric field $\mathbf{E}$ and the position operator $\mathbf{r}$ are both parity-odd and time-even vectors. For H_A the vector potential $\mathbf{A}$ and momentum $\mathbf{p}$ are both parity-odd and time-odd vectors. So according to the electronic selection rules, one-body TRSR will not allow H_E to induce an intra-configuration transition, but will allow H_A to. The PSR, however, forbids both H_E and H_A to give such a transition.

The similar analyses can also be made for other interaction Hamiltonians and the results are listed in table 6.1. In this table, $\surd$ ($\times$) denotes that the intra-configuration transitions induced by corresponding electronic operator are (are not) allowed by the selection rule. Among these interaction operators, only H_B and H_L can have intra-configuration transitions in first-order of perturbation, which are allowed by both the PSR and the TRSR.

Table 6.1, Spacetime symmetry of electronic matter-field interaction operators

	E1 operators					M1 operators		
	H_A	H_E	H_T	H'_S	H_p	H_L	H_B	H''_S
	$\mathbf{p}$	$\mathbf{r}$	$\mathbf{s}\times\mathbf{r}$	$\mathbf{s}\times\mathbf{p}$	$\mathrm{i}(\mathbf{r}\cdot\mathbf{p})\mathbf{p}$	$\mathbf{l}$	$\mathbf{s}$	$\mathrm{i}\mathbf{s}$
Parity	odd	odd	odd	odd	odd	even	even	even
Time	odd	even	odd	even	odd	odd	odd	even
PSR	$\times$	$\times$	$\times$	$\times$	$\times$	$\surd$	$\surd$	$\surd$
TRSR	$\surd$	$\times$	$\times$	$\surd$	$\surd$	$\surd$	$\surd$	$\times$

6.3 Applications for spin-forbidden transitions

6.3.1 Intra-configuration spin-forbidden transitions

Now we choose some practical optical transition processes as examples. The discussion will be restricted to the length gauge. As we have mentioned at the beginning of this chapter, the nominal spin-forbidden transitions are widely observed in the heavier elements in the states of atomic, molecular, and the lanthanide ions in crystals and solutions. For example, the strong 577.0 (nm) and 579.0 (nm) yellow emission lines

of mercury atoms are such nominal spin-forbidden transitions $(6s6d)^3D_2 - (6s6p)^1P_1$ and $(6s6d)^3D_1 - (6s6p)^1P_1$ respectively. Similar spin-forbidden transitions are also observed in lanthanide (ions) before and after embedding into crystals (see e.g. Hufner (1978)). These phenomena are explained by intermediate coupling, when pure LS-coupling (Russell-Saunders coupling) states with different spin-dependence can be further coupled (see e.g. Wybourne (1960, 1961)). Therefore the LS-coupling assignment for states, such as $^3D_1$, is an approximate description of a mixture of different LS-coupling states which is labelled by the dominant component (more than 80%). Hence in original Judd-Ofelt theory, the "spin-forbidden" transitions among these mixed states were calculated, although the effective operator of the original Judd-Ofelt theory is spin-independent. On the other hand, since the labelled component dominates, any spin-dependent interaction operator, giving a *direct link* between two dominant components with different spin, would be important.

As we shown in section 6.1, within a one-particle system in a central field, an important relativistic correction for the electron Hamiltonian is the spin-orbit interaction $V_{SO} = \zeta \mathbf{s} \cdot \mathbf{l}$. For a many-particle system with a central potential, it can be written as $V_{SO} = \lambda \mathbf{S} \cdot \mathbf{L}$ where $\mathbf{S} = \sum_i \mathbf{s}_i$, and $\mathbf{L} = \sum_i \mathbf{l}_i$ (see e.g. Bethe and Salpeter 1957, and Stedman 1990). In a many-particle system, a reasonable approximation and simplification for the relativistic perturbation corrections can be taken as the additive one-particle relativistic spin-correction terms. It means that interactions such as the spin-other-orbit, spin-spin, and orbit-orbit interactions, which come from relativistic Breit interaction, are omitted.

As initially suggested by Wybourne (1968), a third-order perturbation could involve a spin-orbit interaction to form an even-parity optical transition operator which is an effective spin-dependent operator and therefore could give a more *direct link* among the nominal spin-forbidden states within the same configuration than second-order Judd-Ofelt spin-independent operators. Judd and Pooler (1982) gave a first attempt at a quantitative calculation. Downer *et al.* (1988) and Burdick *et al.* (1989) gave a fuller analysis of such third-order perturbation. It is noted that in their (Downer *et al.*) calculations, only the dominant component states are calculated for such third-order effect, i.e. intermediate coupling was ignored. These third-order spin-forbidden effects were compared with the original Judd-Ofelt results in their papers (e.g. table 1 of Downer *et al*). Some particular spin-forbidden transitions were discussed for Eu^{3+}, Gd^{3+}, etc.

In addition, as having been proved in sections 6.1 and 6.2 in both the velocity and the length gauge, we do have a spin-dependent matter-field interaction H'_S even in the E1 limit. Its possible importance to induce a direct intra-configurational spin-forbidden transition in a lower order of the perturbation will also be discussed in this section. In this case, since the transition is an intra-configurational transition, the TRSRs obtained in chapter 4 and in particular the TRSR appropriate for perturbation case (see section 5.1 of chapter 5) are applicable and important.

The third-order mechanism, followed up by Downer *et al.* (1988) and Burdick *et al.* (1989), can be written as

$$M_{gf}^{(3)} = \sum_{m,n}[\frac{\langle g|H_E|n\rangle\langle n|V_{SO}|m\rangle\langle m|V_O|f\rangle}{(E_f - E_m)(E_f - E_n)} + \frac{\langle g|V_O|n\rangle\langle n|V_{SO}|m\rangle\langle m|H_E|f\rangle}{(E_g - E_m)(E_g - E_n)}]. \quad (6.32)$$

We have $E_f = E_g + \hbar\omega$, $E_m = E_n = E_g + \Delta$. Four other third-order terms are omitted here for simplicity. The corresponding Goldstone diagram for this third-order perturbation is diagram (b) in Fig. 2.8. Hence, the effective operator can be defined as

$$\hat{A}_e = \sum_{m,n}[\frac{H_E|n\rangle\langle n|V_{SO}|m\rangle\langle m|V_O}{(\Delta - \hbar\omega)^2} + \frac{V_O|n\rangle\langle n|V_{SO}|m\rangle\langle m|H_E}{\Delta^2}]. \quad (6.33)$$

It acts between the initial (g) and final (f) states (within the model space according to the definition given in chapter 2) only. Since these two terms have different energy denominators, $\hat{A}_e$ is not hermitian. It corresponds to a single photon annihilation process. $\hat{A}_e$ can be symmetrised and anti-symmetrised as

$$\hat{A}_{e\pm}^{\pm} = \sum_{m,n}[H_E|n\rangle\langle n|V_{SO}|m\rangle\langle m|V_O \pm V_O|n\rangle\langle n|V_{SO}|m\rangle\langle m|H_E]C_{\pm}, \quad (6.34)$$

where $C_{\pm} = \frac{1}{2}[\frac{1}{(\Delta-\hbar\omega)^2} \pm \frac{1}{\Delta^2}]$, and as before the subscript + (−) denotes the symmetrised hermitian (antisymmetrised antihermitian) part, and the superscript + (−) refers to HT-even (HT-odd) operator respectively. Since H_E, V_{SO}, and V_O are all time-even, the hermitian part has the HT signature $\tau_{e+} = +1$, i.e. $\hat{A}_{e+}^{+}$. The antihermitian part has the HT signature $\tau_{e-} = -\tau_{e+} = -1$, i.e. $\hat{A}_{e-}^{-}$. According to eqns. (5.5), (5.8) and (5.9) and with a simple extension to the above third-order effective operator, we have the TRSR

$$\tau_{e\pm} = (-1)^{\kappa+k}, \quad (6.35)$$

where κ and k are the spin and orbital ranks of the coupled effective tensor operator $\mathbf{W}^{(\kappa,k)}$, respectively. According to this TRSR, eq. (6.35), the sum of the coupled

spin-orbital ranks, $\kappa + k$, of the time-even hermitian A^+_{e+} (time-even anti-hermitian $\hat{A}^-_{e-}$) part can only be even (odd), i.e. $\hat{A}^+_{e+}$ ($\hat{A}^-_{e-}$) gives the effective tensor operators $\mathbf{W}^{(\kappa,k)}$ with $\kappa + k =$ even (odd respectively). Since V_{SO} and H_E do not commute, the tensor cancellation selection rule (see eq. 5.23 in section 5.3) based on tensor coupling will not apply. Hence both A^+_{e+} and $\hat{A}^-_{e-}$ are expected to give the contribution.

By using the second quantisation method, Downer *et al.* (1988) obtained various effective tensor operators $\mathbf{W}^{(\kappa,k)}$ without specifying their HT symmetries. In a private communication, Burdick pointed out: "*I have come to the conclusion that there is no conflict between the TRSR and my formulation of the spin-orbit terms. First, the one-body operator* $\zeta_d \boldsymbol{W}^{(\kappa,k)t}$ *exactly obeys the time reversal selection rule.* $\cdots$ *The remaining term, however, is the subject of the contention. The solution, I believe, comes in the realization that this term* $\zeta_f \boldsymbol{W}^{(\kappa,k)t}$ (with $\kappa + k =$ odd) *does not come from a simple one-body operator, but rather from a commutator of two operators.* $\cdots$ *This is just a "hand-waving" argument. I hope you can show this in a more rigorous manner.*" Here the spin-orbit interaction parameter ζ (also used in their paper) is equivalent to our notation λ. ζ_f and ζ_d mean that the spin-orbit interaction acts within the ground $4f^N$ and the intermediate $4f^{N-1}n'd$ configuration respectively.

We can see from eqns. (6.32) and (6.34) that indeed the antisymmetrised form of $\hat{A}^-_{e-}$ will reduce to a commutator under a strong closure approximation (see below). Since it is HT-odd, the TRSR will require $\kappa + k$ to be odd. The only difference is that if we assume that the intermediate states $|m\rangle$ and $|n\rangle$ belong to the configuration $nf^{N-1}n'd$, the resulting effective tensor operators of $\hat{A}^-_{e-}$ would be $\zeta_d \mathbf{W}^{(\kappa,k)t}$ with $\kappa + k =$ odd, instead of ζ_f operator.

In another private communication, Judd (1992) commented on our preprinted paper (Wang and Stedman 1993): "$\cdots$ *the production of a new term* H_T *is fascinating, and I ask myself where it could come from. In anticipating objection, you brought up the question of its being second order rather than third order. However, I can produce your* H_T *term if I take* H_A *plus the spin-orbit interaction and the odd parity crystal field* V_O *to third order. So your analysis should agree with that of Downer to third order (and, if so, to my work with Pooler, which Downer reworks).*" "*PPS: On reflection, there could be substantial differences with Downer because he did not use as complete a closure as* $\sum_b |b\rangle\langle b| = 1$.*"*

In order to clarify Burdick and Judd's arguments and in particular to see how a new spin-dependent H_T operator can be re-produced from third-order perturbation,

we investigate the antisymmetrised operator $\hat{A}^{-}_{e-}$ in detail. Assume the intermediate states m and n in eq. (6.32) belong to the configuration $4f^{N-1}n'd$ and the spin-orbit interaction acts within it, we apply the strong closure approximation (similar to eq. (5.10)) for the intermediate states in eq (6.34).

$$\sum_n |n\rangle\langle n| \sum_m |m\rangle\langle m| = 1. \tag{6.36}$$

This is equivalent to Judd's remark, "use as complete a closure as $\sum_b |b\rangle\langle b| = 1$". Thus the anti-hermitian part $\hat{A}^{-}_{e-}$ indeed reduces to a commutator and we obtain

$$\begin{aligned} \hat{A}^{-}_{e-} &= [H_E V_{SO} V_O - V_O V_{SO} H_E] C_- = [-e\mathbf{E}\cdot\mathbf{r}, \lambda_d \mathbf{L}\cdot\mathbf{S}] V_O C_- \\ &= -e\lambda_d \mathbf{E}\cdot[\mathbf{r}, \mathbf{L}\cdot\mathbf{S}] V_O C_- = -ie\lambda_d \hbar (\mathbf{E}\cdot\mathbf{S}\times\mathbf{r}) V_O C_-. \end{aligned} \tag{6.37}$$

The electromagnetic field is taken as the negative frequency component corresponding to photon absorption,

$$\mathbf{A} = \mathbf{A}_0 e^{-i\omega t}, \text{ and } \mathbf{E} = -\partial\mathbf{A}/\partial t = i\omega\mathbf{A},$$

the anti-hermitian part can then be written as

$$\hat{A}^{-}_{e-} = -\hbar\omega H_T V_O C_- \tag{6.38}$$

where $H_T \equiv -e\lambda_d \mathbf{A}\cdot\mathbf{S}\times\mathbf{r}$ (see eq 6.13). The operator $H_T V_O$ is a time-odd hermitian operator and its HT signature is -1. This is in agreement with $\tau^e_- = -1$. Hence the coupled effective tensor operators will be $\lambda_d \mathbf{W}^{(\kappa,k)}$ with $\kappa + k =$ odd according to the TRSR (eq. 6.35). This proves Judd's remark that H_T can be reproduced from third-order perturbation, which may also be substantially different from Downer's result by noting that such HT-odd operator could also have the spin-orbit interaction within the intermediate configuration. It also proves Burdick's comment that such HT-odd operators with $\kappa+k =$ odd come from a commutator reduced from an antisymmetrised operator.

Since we have proved that H_T is cancelled out in the length gauge as a first-order operator, it is very interesting to note that it reappears from a commutator in third-order perturbation. This HT-odd operator plays a role in addition to the HT-even hermitian part $\hat{A}^{+}_{e+}$, and below we will show its importance from the TRSR and from experiment.

Since the transition is intra-configuration transition, i.e. the initial and final states belong to the same configuration, the TRSRs can be applied and restrict the

spin-orbital ranks of $\hat{A}^{+}_{e+}$ and $\hat{A}^{-}_{e-}$ quite differently. There is no restriction on the final coupling rank t in SO^{J}_{3} of $\mathbf{W}^{(\kappa,k)t}$. According to Wybourne (1968) the final coupled rank t is restricted by the tensor product rules, and for the $\hat{A}^{+}_{e+}$ term t is restricted to be *even* only. According to the TRSR (eq. 6.35), the effective tensor operators $\mathbf{W}^{(1,1)}$, $\mathbf{W}^{(1,3)}$, and $\mathbf{W}^{(1,5)}$ must come from the HT-even part $\hat{A}^{+}_{e+}$. And $\mathbf{W}^{(1,2)}$, $\mathbf{W}^{(1,4)}$, and $\mathbf{W}^{(1,6)}$ used by Downer *et al.* (1988) are allowed to be only HT-odd operators, and so must come from $\hat{A}^{-}_{e-}$. The spin-orbit interaction V_{SO} in these HT-odd operators can act not only within the ground configuration $4f^{N}$ (other four terms not included in eq. 6.32) but also within the intermediate configuration. Evidently, we recover all of the effective tensor operators obtained by Downer *et al.* (1988) and Burdick *et al.* (1989) from a different viewpoint, and can assign them with different HT signatures, physical origins, and effects.

Furthermore, considering spin-forbidden transitions within Gd^{3+}, experiment demonstrates the importance of that HT-odd part $\hat{A}^{e}_{-}$ over the HT-even part $\hat{A}^{e}_{+}$. Following Downer *et al.* we omit intermediate coupling. A fuller analysis including intermediate coupling should be done if the qualitative effect of this theory are to be obtained reliably; this was beyond the aim of this project. Since the ground manifold ${}^{8}S_{\frac{7}{2}}$ is an nominal orbital singlet, the orbital rank k of the operator should equal to the orbital rank L of the excited state. Hence, the transitions to ${}^{6}P_{J}$ are induced largely by an HT-even effective operator since $\kappa + k = 1 + 1 = 2$, while those to ${}^{6}D_{J}$, ${}^{6}F_{J}$, and ${}^{6}I_{J}$ are all induced largely by an HT-odd effective coupling, since they correspond to $\kappa + k = 1 + 2$, $1 + 4$, and $1 + 6$ respectively. The experimental results shown (see e.g. Downer *et al.* 1988) that the transition lines ${}^{6}D_{J}$, ${}^{6}F_{J}$, and ${}^{6}I_{J}$ are much stronger than the transition line ${}^{6}P_{J}$. This fact can be explained qualitatively by noting that $\hat{A}^{e}_{-}$ provides a more *direct link* between these dominant spin-forbidden states than the $\hat{A}^{e}_{+}$ part, since H_{T} is a direct spin-dependent matter-field interaction.

We now point out that a further E1 contribution to spin-forbidden transition strengths is to be expected in view of the results of sections 6.1 and 6.2: the interaction H'_{S} (eq. 6.17) in the length gauge is also of comparable order of magnitude to the spin-orbit coupling and could in one step introduce both a spin and a parity change into the atomic states. This suggests the value of exploring the second order effective operator:

$$\hat{B}^{e} = \sum_{m}[\frac{|H'_{S}|m\rangle\langle m|V_{O}|}{(\Delta - \hbar\omega)} + \frac{|V_{O}|m\rangle\langle m|H'_{S}|}{(\Delta)}]. \tag{6.39}$$

Since $H'_S = \alpha \mathbf{E}\cdot\mathbf{S}\times\mathbf{p}$ and V_O (odd rank crystal field) are time-even operators. Under palindromic symmetrisation/antisymmetrisation it can be written as

$$\hat{B}^{\pm}_{e\pm} = \sum_m [H'_S|m\rangle\langle m|V_O \pm V_O|m\rangle\langle m|H'_S]C_{\pm}, \tag{6.40}$$

and $\hat{B}^{+}_{+}$ and $\hat{B}^{-}_{-}$ are HT-even and HT-odd operators respectively. Furthermore, since H'_S and V_O commute, the tensor cancellation selection rule under approximations is applicable.

According to eq. (5.24) and the discussion in section 5.3, for palindromic symmetrised part we have

$$\hat{B}^{+}_{e+} \simeq [1+(-1)^{\kappa_1+\kappa_2+k_1+k_2}]\mathbf{W}^{(\kappa,k)}_{\pi,q}. \tag{6.41}$$

According to eq. (5.26), for antisymmetrised part we obtain

$$\hat{B}^{-}_{e-} \simeq [1+(-1)^{\kappa_1+\kappa_2+k_1+k_2}]\mathbf{W}^{(\kappa,k)}_{\pi,q}. \tag{6.42}$$

Hence for both $\hat{B}^{+}_{e+}$ and $\hat{B}^{-}_{e-}$, the near cancellation condition is that $\kappa_1+\kappa_2+k_1+k_2$, the sum of the spin-orbital ranks of the component operators is *odd.* Since H_T operator has spin rank 1 and the orbital rank 1, and V_O operator has the odd orbital rank, they satisfy this condition for a near cancellation. These has the effect of reducing the contribution from H'_S to Judd-Ofelt theory more from that of a second-order interaction, whose necessity if present would certainly have been felt before now, to that of the third-order terms such as eq. (6.32) which it more nearly rivals for importance. We suggest that it should be incorporated in analyses of spin-assisted transition intensities alongside the standard mechanisms. Since eq. (6.39) has a very different structure to eq. (6.32) – in particular, it implies that the spin of the transition operator is perpendicular to the polarisation of the photon – its effects may well be clearly distinguishable.

We also note that some of the M1 operators obtained in sections 6.1 and 6.2 can induce the one-step transitions within the same configuration. Their significance compared with others (second- and third-order E1 terms) should also be verified by quantitative calculations.

6.3.2 Inter-configuration spin-forbidden transitions

As mentioned in the beginning of this chapter, for light elements such as helium the spin-orbit interaction is very weak and the LS-coupling is a very good approximation.

The spin-forbidden transitions do not occur under normal circumstances. However, it is known that such spin-forbidden transitions are strong features of the spectra of high-temperature plasma and the solar corona (see Drake and Dalgarno 1968). There has been some discussion of the correct method of evaluating transition matrix elements for spin-forbidden electric-dipole (E1) transitions, such as $1s2p\ ^3P_1 - 1s^2\ ^1S_0$ and $1s2p\ ^3P_1 - 1s2s\ ^1S_0$ transitions of helium (see Drake 1972, 1976).

In E1 limit, neither H_A nor H_E can induce such spin-forbidden transitions and intermediate coupling is negligible. The relativistic spin-corrections must be taken into account in order to mix different spin states. A rather thorough analysis of the relativistic corrections for helium-like atoms presented by Drake (1972) gave the spin-dependent energy corrections for the unperturbed wave functions. He also showed that in the length gauge and in the E1 approximation, the matter-field interaction is H_E even when all relativistic corrections are taken into account. Hence the spin-forbidden transitions in helium are interpreted and calculated by doing relativistic spin-corrections for the unperturbed wavefunctions. We have verified in section 6.2 that in the length gauge, the spin-dependent matter-field interaction H_T is cancelled out exactly (see Drake 1972, 1976). However, we have also shown in sections 6.1 and 6.2 that even in a one-particle system, in E1 limit, another spin-dependent matter-field interaction H'_S not considered by Drake is present. We will briefly discuss its possible importance for inter-configuration spin-forbidden transitions in helium even though our analysis is based on a one-particle system.

In the sense of the approximation made in section 6.3.1, i.e. for a many-particle system, the relativistic corrections are taken as the additive one-particle relativistic spin-correction terms only. We can try the following qualitative discussions in a simplified manner.

It is true for helium atom that the spin-orbit interaction V_{SO} is too weak to mix different spin-states, or say that intermediate coupling is negligible. For an electron within a nucleus central field with the spin angular s and the orbit angular momentum $\mathbf{l}$, the spin-orbit interaction is $V_{SO} = Ze^2\mathbf{s}\cdot\mathbf{l}/8\pi\epsilon_0 m^2c^2r^3$. Even in the case of a high linear speed atom such as the solar corona or high-temperature plasma, the orbit angular momentum $\mathbf{l}$ of the electron would not increase dramatically.

Even so we can still write such possibly very weak mixing of different spin-states in second-order perturbation as the following. For spin-forbidden transition

$1s2p\ ^3P_1 - 1s^2\ ^1S_0$ of helium one can write

$$M^{(2)} = \frac{1}{\Delta}\langle 1s^2;\ ^1S_0|H_E|1s2p;\ ^1P_1\rangle\langle 1s2p;\ ^1P_1|V_{SO}|1s2p;\ ^3P_1\rangle, \tag{6.43}$$

where $\Delta = E(^3P_1) - E(^1P_1) = 2048\ (cm^{-1})$. We note that this is the only second-order matrix element that can exist. For another spin-forbidden transition $1s2p\ ^3P_1 - 1s2s\ ^1S_0$ we may write the corresponding matrix elements as

$$M'^{(2)} = \frac{1}{\Delta}\langle 1s2s;\ ^1S_0|H_E|1s2p;\ ^1P_1\rangle\langle 1s2p;\ ^1P_1|V_{SO}|1s2p;\ ^3P_1\rangle. \tag{6.44}$$

On the other hand, we propose that spin-dependent operator H'_S can induce these spin-forbidden transitions in one-step in first-order perturbation as

$$M^{(1)} = \langle 1s^2;\ ^1S_0|H'_S|1s2p;\ ^3P_1\rangle, \tag{6.45}$$

$$M'^{(1)} = \langle 1s2s;\ ^1S_0|H'_S|1s2p;\ ^3P_1\rangle. \tag{6.46}$$

Since they are inter-configuration transitions, parity-odd and time-even operator H'_S is allowed by parity selection rule. The intra-configurational TRSRs are not applicable in this case. Since the $H'_S = -e\mathbf{E}\cdot\mathbf{s}\times\mathbf{p}/2m^2c^2$, the electronic part can be presented by a tensor operator $\mathbf{W}^{(1,1)1}$. Since H'_S is proportional to the linear momentum $\mathbf{p}$ of the electron, we can expect that this operator increase dramatically in a high-speed atom, and thus gives an important (and simple) contribution to such spin-forbidden transitions in high speed. We can see that H_T gives a natural and simple qualitative explanation of the spin-forbidden transition in solar corona and high-temperature plasma.

The full importance of this one-step spin-forbidden transition should be verified by a quantitative calculation which is beyond the scope of this thesis.

Recently, in a private communication, Professor B. R. Judd (1993) has made an elegant quantitative calculation which shows a similar comparison between the spin-orbit interaction assisted (similar to eqns. 6.43 and 6.44) and the new operator H'_S induced transitions (similar to eqns. 6.45 and 6.46), but for a hydrogen-like atom,

$$R = \frac{\langle 1s\ \overset{+}{0}\ |\ H_E\ |3p\ \overset{+}{0}\rangle\ \langle 3p\ \overset{+}{0}\ |\ V_{SO}\ |2p\ \bar{1}\rangle}{(E_{2p} - E_{3p})\ \langle 1s\ \overset{+}{0}\ |\ H'_S\ |2p\ \bar{1}\rangle}. \tag{6.47}$$

He said: "*I couldn't resist seeing how important the spin-orbit mixing of* $3p$ *into* $2p$ *is, compared to the effect of your new operator, in calculating the intensity of transition from spin-up state of* $1s$ *in a hydrogenlike atom to the* $m_l = 1$*, spin-down state of*

$2p$. *It turns out that there is a significant correction (the ratio R is about -0.3).*" His quantitative calculation suggests that the operator H'_S plays an important role in this transition. So we would also expect the same effect for the helium case.

CHAPTER 7

Ground state splittings and MCD in half-filled shells

Atoms with half-filled shells ($N = 2l + 1$) have special properties. Many of these properties were originally noted by Racah (1943). For example he noted that in the case of half-filled shell, the spin-orbital tensor operator $T^{(\kappa,k)}$ with even $\kappa + k$ has zero matrix element between two states with the same *seniority* representation v.

The many-electron states in a half-filled shell can be classified into two classes, Class I whose zero-order eigenfunctions change sign under charge conjugation, and Class II that do not change. These two classes can be distinguished by their seniority v, i.e. the irrep of the symplectic group Sp_{4l+2}. For Class I states the seniority $v = N, N-4, \cdots$, and for Class II states $v = N-2, N-6, \cdots$. The spin-orbit interaction and the even parity crystal field cannot have non-zero matrix elements within the same classes, and the Coulomb interaction cannot have non-zero matrix elements between two different classes.

Quasi-spin Q was introduced into atomic physics in the 1960s (see e.g. Judd 1967). By using the quasi-spin classification in terms of group theory, these magic properties of half-filled shell can be satisfactorily explained. Many works have extended this, e.g. Wybourne (1973) to ligand field theory. Stedman (1987) extended this work to other fields and discussed the formal linkage between selection rules associated with quasi-spin and charge conjugation on the one hand, and time reversal selection rules on the other. Wybourne (1991) gave a recent review and a clear discussion of quasi-spin classification for atomic states and operators in group theory.

We can use systems with half-filled shells to investigate some special effects which normally are hidden. The point is that for half-filled shells the above rules ensure that many first- and second-order effects vanish making it possible to observe the higher

order effects. For example, the ground state can only be mixed up with other states via (for example) the spin-orbit interaction by third-order or higher order perturbation, or the degeneracy of such ground state can only be lifted by crystal field by going to third-order, and higher in the case of cubic symmetry.

Matrix isolation spectroscopy, especially in noble-gas matrices, has become a widely used technique for studying various species. A chemically inert matrix traps the reactive species, preventing further reactions, but does not exert any strong influence on the isolated species, leaving its properties nearly unchanged. There is no such ideal matrix and therefore one always finds matrix-induced changes in the spectra which manifest themselves in level shifts, or additional splitting. Thus a thorough knowledge of the cage effect on the isolated species is important for analysis of the spectra.

Recently there has been considerable experimental and theoretical work on the application of magnetic circular dichroism (MCD) to these matrix isolated systems. Much of this latter work has centred around moment analysis of the absorption spectra of these systems. Our attention to this work was drawn in particular by the claim of Pellow *et al.* (1989) to have successfully deduced the ground state splitting of atomic rhenium in krypton matrix from a series of MCD measurements.

We wish to discuss the severe problems that arise in using MCD to deduce and interpret a ground state splitting especially in the case of a half filled shell (see Wang and Wybourne 1990). Many of these shortcomings arise from a failure to address fully the properties of the isolated atoms, especially the half-filled shell elements prior to their insertion in matrices.

7.1 Quasi-spin, quasi-spin selection rule, and special properties of half-filled shells

Here we briefly review the quasi-spin classification of the states and operators and the quasi-spin selection rule for half-filled shells. An excellent review is that of Wybourne (1991). The following accounts are based on this article.

The quasi-spin operators are defined by Judd (1967) as scalar-coupled spherical creation and annihilation operators

$$\begin{aligned} Q_+ &= \frac{1}{2}\sqrt{(4l+1)}\,[\mathbf{a}^\dagger\mathbf{a}^\dagger]^{(00)}, \\ Q_- &= -\frac{1}{2}\sqrt{(4l+1)}\,[\mathbf{aa}]^{(00)}, \end{aligned} \tag{7.1}$$

$$Q_Z = \frac{1}{4}\sqrt{(4l+1)}\,([\mathbf{a}^\dagger\mathbf{a}]^{(00)} + [\mathbf{a}\mathbf{a}^\dagger]^{(00)}).$$

These operators satisfy the commutation relations

$$[Q_Z, Q_\pm] = \pm Q_\pm; \quad [Q_+, Q_-] = 2Q_Z \tag{7.2}$$

which correspond to the Lie algebra associated with a quasi-spin group SU_2^Q analogous to the spin group SU_2^S. Thus $Q_\pm$ and Q_Z can be regarded as forming the components of a quasi-spin $\mathbf{Q}$. In group theory, this quasi-spin group SU_2^Q can be embedded into a group chain as

$$U_{2^{4l+2}} \supset SO_{8l+5} \supset SO_{8l+4} \supset SU_2^Q \times [Sp_{4l+2} \supset SU_2^S \times (SO_{2l+1} \supset SO_3^L)]. \tag{7.3}$$

The quasi-spin operators acting on the states have the eigenvalues

$$Q_Z\,|l^N, vSLM_SM_L\rangle = M_Q\,|l^N, vSLM_SM_L\rangle, \tag{7.4}$$

$$Q_-\,|l^N, vSLM_SM_L\rangle = 0, \tag{7.5}$$

$$\mathbf{Q}^2\,|l^N, vSLM_SM_L\rangle = Q(Q+1)\,|l^N, vSLM_SM_L\rangle, \tag{7.6}$$

with

$$M_Q = \frac{1}{2}(2l+1-N); \quad Q = \frac{1}{2}(2l+1-v). \tag{7.7}$$

The irreps (Q, M_Q) of SU_2^Q carry the same information as (N, v). Q may be regarded as measuring the distance from the centre of a shell to a given seniority state. M_Q measuring the filling up of the shell with respect to the centre (half-filled shell). For half-filled shell, $N = 2l+1$, and thus $M_Q = 0$.

The electron states can be classified according to this group chain. Such classification for d^N electrons is given in tables 7.1 for even number electrons and in 7.2 for odd number electrons.

The operators can also be classified accordingly. The spherical creation and annihilation operators $\mathbf{a}^\dagger$ and $\mathbf{a}$ transform as the irrep $q = 1/2$ of SU_2^Q with $m_q = \pm 1/2$. Thus each $\mathbf{a}$ (or $\mathbf{a}^\dagger$) can form a component *triple tensor operator* $\mathbf{a}^{(qsl)}$ ($\mathbf{a}^{\dagger(qsl)}$) with well defined quasi-spin rank $q(=1/2)$, spin rank $s(=1/2)$, and orbital rank l respectively. By using the standard vector-coupling method, $\mathbf{a}^{(qsl)}$ and $\mathbf{a}^{\dagger(qsl)}$ can produce irreducible triple tensor operators with well defined total quasi-spin Q (denoted as the quasi-spin rank K). For example, a one-body irreducible triple tensor operator $\mathbf{X}^{(K,\kappa,k)}$ can be defined as

$$\mathbf{X}^{(K,\kappa,k)} \equiv [\mathbf{a}^{\dagger(qsl)}\mathbf{a}^{(qsl)}]^{(K,\kappa,k)}. \tag{7.8}$$

Table 7.1 Quasi-spin classification for d^N configuration for even N

SO_{20}	Q	M_Q	N	v	Sp_{10}	SO_5	^{2S+1}L
Δ_+	1/2	1/2	6	4	$\langle 1^4 \rangle$	[1]	^5D
						[21]	^3PDFGH
						[22]	^1SDFGI
		−1/2	4			[1]	^5D
						[21]	^3PDFGH
						[22]	^1SDFGI
	3/2	3/2	8	2	$\langle 11 \rangle$	[11]	^3PF
						[2]	^1DG
		1/2	6			[11]	^3PF
						[2]	^1DG
		−1/2	4			[11]	^3PF
						[2]	^1DG
		−3/2	2			[11]	^3PF
						[2]	^1DG
	5/2	5/2	10	0	$\langle 0 \rangle$	[0]	^1S
		3/2	8			[0]	^1S
		1/2	6			[0]	^1S
		−1/2	4			[0]	^1S
		−3/2	2			[0]	^1S
		−5/2	0			[0]	^1S

It can be proved (see e.g. Wybourne 1991) that the one-body operators $[\mathbf{a}^\dagger \mathbf{a}]^{(\kappa,k)}$ with $\kappa + k = odd$ have quasi-spin $K = 0$ while $\kappa + k = even$ have quasi-spin $K = 1$. Thus according to the one-body time reversal selection rule (eq. 3.29) this conclusion can be easily translated as: *the time-odd one-body operators have quasi-spin* $K = 0$ *while the time-even one-body operators have quasi-spin* $K = 1$.

For the two-body Coulomb interaction, its quasi-spin rank $K = 0, 2$. I cannot generalise the two-body case in terms of time reversal symmetry of the two-body operator at the moment. I believe that by using the time reversal argument it is possible to give an explanation.

Now we can discuss the quasi-spin selection rule for half-filled shell. According to the Wigner-Eckart theorem a matrix element written in terms of well defined quasi-

Table 7.2 Quasi-spin classification for d^N configuration for odd N

SO_{20}	Q	M_Q	N	v	Sp_{10}	SO_5	^{2S+1}L
	0	0	5	5	$\langle 1^5 \rangle$	[0]	^6S
		1	7			[11]	^4PF
						[21]	^2PDFGH
	1	0	5	3	$\langle 1^3 \rangle$	[11]	^4PF
						[21]	^2PDFGH
Δ_-		−1	3			[11]	^4PF
						[21]	^2PDFGH
		2	9			[1]	^2D
		1	7			[1]	^2D
	2	0	5	1	$\langle 1 \rangle$	[1]	^2D
		−1	3			[1]	^2D
		−2	1			[1]	^2D

spin of both the states and the operator can be expressed as

$$\langle \alpha Q M_Q | X^{(K,\kappa,k)}_{\sigma\pi q} | \alpha' Q' M'_Q \rangle = (-1)^{Q-M_Q} \begin{pmatrix} Q & K & Q' \\ -M_Q & \sigma & M'_Q \end{pmatrix} \langle \alpha Q || X^{(K,\kappa,k)}_{\pi q} || \alpha' Q' \rangle. \tag{7.9}$$

According to eq. (7.7), since Q is independent of N, the number of electrons, and $M_Q = -(2l+1-N)/2$, we conclude that the matrix element is only dependent on a single 3jm symbol since the reduced matrix element is independent of N.

For a half-filled shell $M_Q = 0$ and hence we have

$$\langle \alpha Q 0 | X^{(K,\kappa,k)}_{0\pi q} | \alpha' Q' 0 \rangle = (-1)^{Q} \begin{pmatrix} Q & K & Q' \\ 0 & 0 & 0 \end{pmatrix} \langle \alpha Q || X^{(K,\kappa,k)}_{\pi,q} || \alpha' Q' \rangle. \tag{7.10}$$

To have this matrix element non-zero, it is necessary that

$$Q + Q' + K \quad \text{be even.} \tag{7.11}$$

Inspection of eq. (7.7) we finally obtain the quasi-spin selection rule for a half-filled shell that *a matrix element of a triple tensor operator with quasi-spin K between states with quasi-spin Q and Q' will vanish unless*

$$\Delta Q = \pm K \quad or \quad \Delta v = \pm 2K. \tag{7.12}$$

The formula $\Delta v = \pm 2K$ is more easy to use since we only need to examine the change of the seniority Δv of the states. According to this selection rule, the special properties of half-filled shell can be easily explained.

As mentioned at the beginning of this chapter, half-filled d-shell d^5 states can be divided into two classes according to their irreps of Sp_{10} as

v	Class I	v	Class II
5	${}^6S\,{}^4DG\,{}^2SDFGI$	3	${}^4PF\,{}^2PDFGH$
1	${}^2D$		

Since time-even crystal and spin-orbit interactions have quasi-spin $K = 1$ and $2K = 2$, they cannot have non-zero matrix elements within the same classes, but can be non-zero between two different classes. On the other hand, since the Coulomb interaction has $K = 0, 2$ and $2K = 0, 4$, it can be non-zero within the same classes, but must be zero between two classes.

7.2 Groundstate splittings of half-filled shell rhenium atom measured by MCD

Pellow and Vala (1989) reported the measurement of the ground state splitting of neutral atomic rhenium (ReI) in a krypton (Kr) matrix by the observation of the saturation phenomena of magnetic circular dichroism (MCD), which gives a splitting of $\sim 7 \pm 3cm^{-1}$. Their experiment is model dependent to the extent that cubic symmetry of the matrix is assumed rather than explicitly deduced by experiment. They suggest that their observed splitting comes from the admixing, via the spin-orbit interaction, of some ${}^4P_{5/2}$ state into the ${}^6S_{5/2}$ ground state of the $5d^56s^2$ electron configuration. We wish to point out that such a mechanism cannot lead to a ground state splitting and show that higher order mechanisms are required.

The admixing of two states ${}^4P_{5/2}$ and ${}^6S_{5/2}$ via the spin-orbit interaction in second-order perturbation is determined by a 2×2 matrix,

$$\begin{bmatrix} \langle {}^4P_{5/2}|H_{SO}|{}^4P_{5/2}\rangle & \langle {}^4P_{5/2}|H_{SO}|{}^6S_{5/2}\rangle \\ \langle {}^6S_{5/2}|H_{SO}|{}^4P_{5/2}\rangle & \langle {}^6S_{5/2}|H_{SO}|{}^6S_{5/2}\rangle \end{bmatrix}.$$

Since the spin-orbit interaction H_{SO} cannot have non-zero matrix element within the same classes, the diagonal elements of the matrix must be zero. Thus these two states cannot mix together by such simple second-order mechanism. To establish a reliable mixed ground state a higher order perturbation mechanism must be invoked. We know that for heavier elements the spin-orbit interaction is strong enough to couple

different states with the same J value. In addition, the configuration interaction can also be significant to give a contribution to mix different configurations, such as $d^{N-2}s^2, d^{N-1}s, d^N$ for neutral atoms.

To obtain such a realistic ground state we were fortunate in having Dr. J. Sugar (1989), of N.I.S.T, Washington, diagonalise the complete $(5d+6s)^7$ energy matrices, including all electrostatic and spin-orbit terms, for parameters appropriate to ReI atomic energy levels derived by a least squares fitting procedure. This leads to the result that the real ground state wavefunction $|^6S_{5/2}\rangle$ is

$$\begin{aligned} |^6S_{5/2}\rangle \;=\; & \{s|^6S\rangle + p|^4P\rangle + d|^4D\rangle + f|^4F\rangle + g|^4G\rangle\} + [d'|^6D\rangle + p'|(^3_4P)\ ^4P\rangle \\ & + p''|(^3_2P)\ ^4P\rangle + d''|(^5D)\ ^4D\rangle + d'''|(^3D)\ ^4D\rangle + f'|(^3_4F)\ ^4F\rangle \\ & + g'|^4G\rangle] + p'''|^4P\rangle + f'''|^4G\rangle. \end{aligned} \tag{7.13}$$

The eigenvector components are

$s = 0.94027,$	$p = 0.31306,$	$d = 0.06939,$	$f = 0.01533,$	$g = 0.00913,$
$d' = 0.00862,$	$p' = 0.01657,$	$p'' = -0.06240,$	$d'' = -0.01480,$	$d''' = -0.01519,$
$f' = -0.00084,$	$f'' = 0.00128,$	$g' = 0.00116,$	$p''' = 0.03127,$	$f''' = 0.00171.$

In this real ground state wavefunction (eq. 7.13) the terms enclosed in braces { } all derive from $5d^56s^2$ configuration, those in square brackets [ ] from $5d^66s$ and the last two from $5d^7$. The $5d^6$ parentage is noted where necessary.

Such a atomic state may be split by a crystal field V_{cry} of the host matrix. A cubic crystal field containing a non-cubic term can be expressed parametrically (see Griffith 1961) as

$$V_{cry} = B_0^2 C_0^{(2)} + B_0^4[C_0^{(4)} + \sqrt{5/14}(C_4^{(4)} + C_{-4}^{(4)})] \tag{7.14}$$

where the B_0^4 term is cubic term and the B_0^2 term is axial. As suggested by Professor M.R. Kibler there is another non-cubic (axial) term

$$D_0^4[C_0^4 - \sqrt{7/10}(C_4^4 - C_{-4}^4)]$$

which is orthogonal to both the terms B_0^2 and B_0^4. This new term could be included in our calculation with no difficulties but for simplicity we only use the eq. (7.14) in the following.

First, we ignore the configuration interaction and only consider the effect within the dominant $5d^5 6s^2$ configuration, i.e. we take an approximate ground state as

$$|^6S'_{5/2}\rangle = s|^6S_{5/2}\rangle + p|^4P_{5/2}\rangle + d|^4D_{5/2}\rangle + f|^4F_{5/2}\rangle + g|^4G_{5/2}\rangle. \tag{7.15}$$

The matrix elements of a tensor operator $C_q^{(k)}$ within the LS-coupling states is calculated by the formula (see Judd 1963)

$$\begin{aligned}&\langle l^N, \alpha SLJM|C_q^{(k)}|l^N, \alpha' SL'J'M'\rangle \\ &= (-1)^{J-M}\begin{pmatrix} J & k & J \\ -M & q & M' \end{pmatrix}\langle \alpha SLJ||U^{(k)}||\alpha' SL'J'\rangle\ \langle l||C^{(k)}||l\rangle\end{aligned} \tag{7.16}$$

where

$$\begin{aligned}&\langle \alpha SLJ||U^{(k)}||\alpha' SL'J'\rangle \\ &= (-1)^{S'+L'+J+K}(2J+1)\begin{Bmatrix} J & k & J \\ L' & S & L \end{Bmatrix}\langle \alpha SL||U^{(k)}||\alpha' SL'\rangle.\end{aligned} \tag{7.17}$$

The matrix elements of the unit tensor operator $\langle \alpha SL||U^{(k)}||\alpha' SL'\rangle$ have been listed by Nielson and Koster (1963), and the reduced matrix element $\langle l||C^{(k)}||l\rangle$ is

$$\langle l||C^{(k)}||l\rangle = (-1)^{2l}(2l+1)\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}. \tag{7.18}$$

We can firstly calculate $\langle \alpha SLJ||U^{(k)}||\alpha' SL'J'\rangle\ \langle d||C^{(k)}||d\rangle$, the reduced matrix elements of the crystal field among the LS-coupling component states of $|^6S'_{5/2}\rangle$ disregarding the 3jm symbol in eq. (7.16). They are listed in Table 7.3 for $k = 2$ and Table 7.4 for $k = 4$.

We can see that the non-vanishing axial and cubic matrix elements are

$$\begin{aligned}&\langle ^4P_{5/2}||C^{(2)}||^4D_{5/2}\rangle,\ \langle ^4D_{5/2}||C^{(2)}||^4F_{5/2}\rangle,\ \langle ^4F_{5/2}||C^{(2)}||^4G_{5/2}\rangle, \\ &\langle ^4P_{5/2}||C^{(4)}||^4G_{5/2}\rangle,\ \langle ^4D_{5/2}||C^{(4)}||^4F_{5/2}\rangle,\ \langle ^4F_{5/2}||C^{(4)}||^4G_{5/2}\rangle.\end{aligned}$$

It is noted that the matrix elements of the crystal field tensor operators (eq. 7.14) vanish within $|^6_5S_{5/2}\rangle + |^4_3P_{5/2}\rangle$ states. This further shows that only considering these two states cannot lead to any such a crystal field splitting.

Now according to eq. (7.16) and tables 7.3 and 7.4 we can calculate the the whole matrix elements of the cubic crystal field B_0^4 term in eq. (7.14) within the

Table 7.3 Reduced matrix elements $\langle \alpha SLJ||U^{(2)}||\alpha' SL'J'\rangle\ \langle d||C^{(2)}||d\rangle$

	${}^6_5S_{5/2}$	${}^4_3P_{5/2}$	${}^4_5D_{5/2}$	${}^4_3F_{5/2}$	${}^4_5G_{5/2}$
${}^6_5S_{5/2}$	0	0	0	0	0
${}^4_3P_{5/2}$	0	0	$6\sqrt{3}/5\sqrt{7}$	0	0
${}^4_5D_{5/2}$	0	$6\sqrt{3}/5\sqrt{7}$	0	$104\sqrt{6}/245$	0
${}^4_3F_{5/2}$	0	0	$104\sqrt{6}/245$	0	45/49
${}^4_5G_{5/2}$	0	0	0	45/49	0

Table 7.4 Reduced matrix elements $\langle \alpha SLJ||U^{(4)}||\alpha' SL'J'\rangle\ \langle d||C^{(4)}||d\rangle$

	${}^6_5S_{5/2}$	${}^4_3P_{5/2}$	${}^4_5D_{5/2}$	${}^4_3F_{5/2}$	${}^4_5G_{5/2}$
${}^6_5S_{5/2}$	0	0	0	0	0
${}^4_3P_{5/2}$	0	0	0	0	$-\sqrt{210}/21$
${}^4_5D_{5/2}$	0	0	0	$5\sqrt{10}/49$	0
${}^4_3F_{5/2}$	0	0	$5\sqrt{10}/49$	0	$-11\sqrt{15}/49$
${}^4_5G_{5/2}$	0	$-\sqrt{210}/21$	0	$-11\sqrt{15}/49$	0

states $|^6\mathcal{S}'JM\rangle$ with $J = 5/2$. The results are listed in Tables 7.5 and 7.6. The coefficients in these two tables are

$$\mathcal{B} = \frac{5\sqrt{70}}{1029}fd - \frac{\sqrt{30}}{63}gp - \frac{11\sqrt{105}}{1029}gf, \quad \mathcal{N} = -\frac{5\sqrt{70}}{343}fd + \frac{\sqrt{30}}{21}gp + \frac{11\sqrt{105}}{343}gf,$$
$$\mathcal{E} = \frac{25\sqrt{14}}{1029}fd - \frac{5\sqrt{6}}{63}gp - \frac{55\sqrt{21}}{1029}gf, \quad \mathcal{Q} = \frac{10\sqrt{70}}{1029}fd - \frac{2\sqrt{30}}{63}gp - \frac{22\sqrt{105}}{1029}gf$$

where $p = 0.31306, d = 0.06939, f = 0.01533, g = 0.00913$ are the eigenvector components of $|^6\mathcal{S}_{5/2}\rangle$ (see eq. 7.13).

For a pure cubic O_h crystal field, according to Griffith (1961), one can construct well defined O_h symmetry function in terms of the ground state wavefunction in the $|JM\rangle$ $(J = 5/2)$ basis and calculate corresponding crystal field splittings. We obtain

Table 7.5 The matrix elements of $\langle {}^6S'5/2\ M|V^{(4)}_{cry}|{}^6S'5/2\ M'\rangle$ for $M, M' = \frac{5}{2}, -\frac{5}{2}, \frac{3}{2}, -\frac{3}{2}$

	$\vert{}^6S'\frac{5}{2}, \frac{5}{2}\rangle$	$\vert{}^6S'\frac{5}{2}, -\frac{3}{2}\rangle$
$\langle {}^6S'\frac{5}{2}, \frac{5}{2}\vert$	$\mathcal{B}B_0^4$	$\mathcal{E}B_0^4$
$\langle {}^6S'\frac{5}{2}, -\frac{3}{2}\vert$	$\mathcal{E}B_0^4$	$\mathcal{N}B_0^4$

	$\vert{}^6S'\frac{5}{2}, -\frac{5}{2}\rangle$	$\vert{}^6S'\frac{5}{2}, \frac{3}{2}\rangle$
$\langle {}^6S'\frac{5}{2}, -\frac{5}{2}\vert$	$\mathcal{B}B_0^4$	$\mathcal{E}B_0^4$
$\langle {}^6S'\frac{5}{2}, \frac{3}{2}\vert$	$\mathcal{E}B_0^4$	$\mathcal{N}B_0^4$

Table 7.6 The matrix elements of $\langle {}^6S'5/2\ M|V_{cry}|{}^6S'5/2\ M'\rangle$ for $M, M' = \frac{1}{2}, -\frac{1}{2}$

	$\vert{}^6S'\frac{5}{2}, \frac{1}{2}\rangle$
$\langle {}^6S'\frac{5}{2}, \frac{1}{2}\vert$	$\mathcal{Q}B_0^4$

	$\vert{}^6S'\frac{5}{2}, -\frac{1}{2}\rangle$
$\langle {}^6S'\frac{5}{2}, -\frac{1}{2}\vert$	$\mathcal{Q}B_0^4$

O_h	Ground state basis	Crystal field splittings $\langle A_\alpha\vert V_{cry}\vert A_\alpha\rangle$
$\vert E''_\alpha\rangle$	$c_1\vert S'\frac{5}{2}, \frac{5}{2}\rangle - c_2\vert S'\frac{5}{2}, -\frac{3}{2}\rangle$	$-2\mathcal{Q}B_0^4$
$\vert E''_\beta\rangle$	$c_1\vert S'\frac{5}{2}, -\frac{5}{2}\rangle - c_2\vert S'\frac{5}{2}, \frac{3}{2}\rangle$	$-2\mathcal{Q}B_0^4$
$\vert U'_\kappa\rangle$	$-c_2\vert S'\frac{5}{2}, -\frac{5}{2}\rangle - c_1\vert S'\frac{5}{2}, \frac{3}{2}\rangle$	$\mathcal{Q}B_0^4$
$\vert U'_\mu\rangle$	$\vert S'\frac{5}{2}, \frac{1}{2}\rangle$	$\mathcal{Q}B_0^4$
$\vert U'_\lambda\rangle$	$-\vert S'\frac{5}{2}, -\frac{1}{2}\rangle$	$\mathcal{Q}B_0^4$
$\vert U'_\nu\rangle$	$c_2\vert S'\frac{5}{2}, \frac{5}{2}\rangle + c_1\vert S'\frac{5}{2}, -\frac{3}{2}\rangle$	$\mathcal{Q}B_0^4$

where $c_1 = 1/\sqrt{6}$ and $c_2 = \sqrt{5/6}$ and again

$$\mathcal{Q} = \frac{10\sqrt{70}}{1029} fd - \frac{2\sqrt{30}}{63} gp - \frac{22\sqrt{105}}{1029} gf. \tag{7.19}$$

Putting in the values yields $\mathcal{Q} = -4.411 \times 10^{-4}$. Thus we obtain a total ground state O_h field splitting of $3\mathcal{Q}B_0^4$ involving just two levels. If $B_0^4 > 0$ then the ground state is U' otherwise it is E''.

If an axial B_0^2 term is included, the degeneracies will change and there will be mixing of some of the E'' and U' levels to give three two-fold degenerate levels. In that case it is essential to also include configuration mixing since the ground states $|{}^6S_{5/2}\rangle$ contains a small, though significant ${}^6D_{5/2}$ component from the $5d^6 6s$ configuration. We have $\langle d^6\ {}^5D, s; {}^6D||V_{cry}||d^5\ {}^6S, s^2; {}^6S\rangle = -B_0'^2$. There is no substantive reason

to expect $B_0'^2 = B_0^2$. Including the non-cubic term B_0^2 and $B_0'^2$ with configuration interaction we take the the ground state as

$$|^6\mathcal{S}''_{5/2}\rangle = s|^6S_{5/2}\rangle + p|^4P_{5/2}\rangle + d|^4D_{5/2}\rangle + f|^4F_{5/2}\rangle + g|^4G_{5/2}\rangle + d'|^6D_{5/2}\rangle. \quad (7.20)$$

Thus we obtain the energy matrices:

	$\|E''_\alpha\rangle$	$\|U'_\nu\rangle$
$\langle E''_\alpha\|$	$-2\mathcal{Q}B_0^4$	$-\frac{\sqrt{5}}{6}\theta B_0^2 - 2sd'\frac{\sqrt{70}}{35}B_0'^2$
$\langle U'_\nu\|$	$-\frac{\sqrt{5}}{6}\theta B_0^2 - 2sd'\frac{\sqrt{70}}{35}B_0'^2$	$\mathcal{Q}B_0^4 - \theta B_0^2 - 4\frac{\sqrt{14}}{35}sd'B_0'^2$

	$\|E''_\beta\rangle$	$\|U'_\kappa\rangle$
$\langle E''_\beta\|$	$-2\mathcal{Q}B_0^4$	$-\frac{\sqrt{5}}{6}\theta B_0^2 - 2sd'\frac{\sqrt{70}}{35}B_0'^2$
$\langle U'_\kappa\|$	$-\frac{\sqrt{5}}{6}\theta B_0^2 - 2sd'\frac{\sqrt{70}}{35}B_0'^2$	$\mathcal{Q}B_0^4 - \theta B_0^2 - 4\frac{\sqrt{14}}{35}sd'B_0'^2$

	$\|U'_\mu\rangle$
$\langle U'_\mu\|$	$\mathcal{Q}B_0^4 + \theta B_0^2 + 4\frac{\sqrt{14}}{35}sd'B_0'^2$

	$\|U'_\lambda\rangle$
$\langle U'_\lambda\|$	$\mathcal{Q}B_0^4 + \theta B_0^2 + 4\frac{\sqrt{14}}{35}sd'B_0'^2$

Where we have

$$\theta = -\frac{24\sqrt{5}}{175}pd - \frac{416\sqrt{70}}{8575}fd - \frac{12\sqrt{105}}{343}fg. \quad (7.21)$$

Putting in the ground state eigenvectors we obtain $\theta = -7.144\times10^{-3}$. Diagonalisation of the matrices yields three distinct eigenvalues

$$\begin{aligned} E_{1,2} &= -\tfrac{1}{2}(\mathcal{Q}B_0^4 + \beta) \pm \tfrac{1}{2}[9\mathcal{Q}^2(B_0^4)^2 - 6\mathcal{Q}\beta B_0^4 + 4\alpha^2 + \beta^2]^{1/2} \\ E_3 &= \mathcal{Q}B_0^4 + \beta \end{aligned} \quad (7.22)$$

where

$$\begin{aligned} \alpha &= -\tfrac{\sqrt{5}}{6}\theta B_0^2 + \tfrac{2\sqrt{70}}{35}sd'B_0'^2 = (2.662B_0^2 - 3.875B_0'^2)\times10^{-3} \\ \beta &= -\theta B_0^2 + \tfrac{4\sqrt{14}}{35}sd'B_0'^2 = (7.144B_0^2 - 3.466B_0'^2)\times10^{-3} \end{aligned} \quad (7.23)$$

The numerical result of the ground state splitting depends on knowing the values of the three parameters $B_0^2, B_0'^2, B_0^4$. At present time these values have not been adequately derived from experimental studies of crystal field energy levels. We have made no attempt to include relativistic effects that are known to be important in half-filled shells (see Wybourne (1965a, 1965b)).

We have tried to show in the preceding remarks that the calculation of the ground state splitting of rhenium atoms in a crystal field is a highly complex matter. The reported splitting, which assumes cubic symmetry, is very large for a half-filled shell. Cubic symmetry always requires a higher order perturbation than non-cubic symmetry with the result that cubic splittings are usually smaller by one to three orders of magnitude than non-cubic splittings. The results of Pellow and Vala (1989) are of great interest and we hope will encourage further experimentation to establish the ground state splitting in detail with much greater precision. An unequivocal experimental determination of the ground state site symmetry will be crucial to the complete analysis of the ground state splitting.

CHAPTER 8

Conclusion

The important role played by the operator of time reversal in physics is further extended in this thesis. The time reversal selection rules of Abragam and Bleaney (1970) and Stedman and Butler (1980) have been extended to the higher group levels in a Racah group chain for atomic physics. In the spin-orbital space, i.e. the product group $SU_2^S \times SO_3^L$, the TRSRs restrict the sum of the spin-orbital ranks of any many-body operators acting within the same electronic configuration to be *even* (*odd*) if the HT signature of the operator is even (odd). This rule can be directly applied to many physical situations similarly to the well known parity selection rule. We show that such rules have been comparatively undeveloped and underutilized in our areas of interest. This TRSR can be easily used, and the results have direct physical meaning. For example, both a position operator $\mathbf{r}$ and a momentum operator $\mathbf{p}$ can be expanded as a rank 1 (or a group) tensor operator, e.g. $\mathbf{r} \sim \mathbf{W}^{(0,1)}$ and $\mathbf{p} \sim \mathbf{W}^{(0,1)}$, but the former has the time reversal signature $+1$ and the latter -1. Thus according to the one-body TRSR, the position operator $\mathbf{r}$ is not allowed to give non-zero matrix elements within a configuration, but the momentum operator $\mathbf{p}$ may give non-zero matrix elements.

According to the Laporte parity rule, both of the operators $\mathbf{r}$ and $\mathbf{p}$ must give vanishing matrix elements within the same configuration. In the case of the electromagnetic interaction, a physical system must be parity and time reversal invariant. The physical operator in such a system must obey both parity and time reversal selection rules. In many cases parity rules are indeed stronger than time reversal rules (when TRSR allows, parity forbids), and thus give the impression that the parity consideration is sufficient. But in general this is not the case. One case where time reversal is stronger than parity can be found in a relativistic correction for the matter-

field interaction H_S'' which has an anti-hermitian electronic operator iS (see chapter 6, Table 6.1). In addition, when the weak interaction is taken into account, parity is no longer conserved, and the Laporte parity rule breaks down. When parity non-conservation was announced, Dirac is reported (Telegdi 1973) to have said: "if you look carefully, you will see that the concept (of parity) is not used in my book". In the parity non-conservation case, time reversal selection rules are expected to play an important role in the field, such as in Sandars' atomic states (Sandars 1977) which are not parity eigenstates. A reliable conclusion draws on the selection rules determined not only by spatial inversion symmetry but also by the HT (hermitian conjugation and time reversal) symmetry. Thus one needs to check both parity and the time reversal restrictions to give a reliable conclusion on the existence of a given matrix element. This does not seem to be well known.

In addition, the time reversal selection rules within a configuration strongly restrict the group symmetry of the operators, such as in the product group $SU_2^S \times SO_3^L$ level mentioned above. At the symplectic group level the symmetry type of the many-body operators is also restricted by the HT signature of the operators. Hence the many-body operators can be classified into two classes as HT-even and HT-odd transforming distinctively as different irreps at that group level. This physical classification plus the group theory method have extra power in dealing with many-body interactions. Such time reversal classifications of many-body operators have been discussed for applications such as Newman's (1971) rule for the ranks of operators contributing to the correlation crystal field within the superposition model. Another application is discussed for the atomic spectrum induced by HT-even spin-independent two-body scalar operators such as the Coulomb and Trees operators. Similar applications come from extending this method to the n-body interaction with $n \geq 3$. A complete group theory calculation for general 3jm in the whole Racah group chain combined with the HT classifications has not been done. Progress on a computer program *RACAH* developed by Dr. P. H. Butler and his students makes such calculations promising in the near future.

The application of the time reversal selection rules in perturbation theory has some complications. An effective operator acting only between the initial and final state must be defined. If and only if such an effective operator has a definite HT-signature under the joint action of hermitian conjugation and time reversal, a definite selection rule can be imposed. Unequal energy denominators in perturbation terms

have an important effect as well as the intermediate states and the closure approximations. The gauge transformation of the Judd-Ofelt theory is discussed in the light of the TRSR. Such analysis has not been fully discussed before.

The extension of the TRSRs from the intra-configurational case to a more general inter-configurational case remains to be done. In fact this is not a very difficult task, and the principles of such extension have been given in section 3.6. Such a extension may lead to a progressive weakening (loss of constraining power) of the resulting TRSR, offset by a corresponding gain – the enlargement of the domain of applicability of that rule.

Dirac theory of the electron – relativistic quantum mechanics – gives some important correction terms such as the well-known spin-orbit interaction for non-relativistic Hamiltonian. Under a re-analysis of the Foldy-Wouthuysen transformation for the Dirac equation, it is found that in fact this relativistic theory also gives corrections for the matter-radiation interaction operators, especially the spin-dependent matter-field interactions. For example, one such correction term is a E1 spin-dependent operator $H'_S = e\dot{\mathbf{A}} \cdot \mathbf{S} \times \mathbf{p}$, and this new light-matter interaction has not been noted before. In addition to H'_S, there are also other new matter-field interactions in both the velocity gauge and the length gauge, and some operators appear in one gauge and disappear in another. The individual importance of these various matter-field interactions and the quantitative comparison between them and between different gauges are interesting problems which remain to be investigated.

Goldstone diagrammatic perturbation methods can be used to discuss the optical transition processes systematically. It is possible to treat the energy level structure problem and the optical transition problem on the same footing in the time-independent context of matrix elements calculation, i.e. we can start with the first-order perturbation V as

$$V = V_2 + V_1; \quad V_2 = V_{Coulomb}; \quad V_1 = V_{SO} + V_{cry} + H_E + H'_S$$

which includes the two-body Coulomb interaction V_2, the one-body spin-orbit interaction V_{SO}, crystal field V_{cry}, matter-field interaction E1 operator in the length gauge $H_E = -e\mathbf{E} \cdot \mathbf{r}$, and a new E1 spin-dependent matter-field interaction discussed in chapter 6 (see Wang and Stedman (1993)) $H'_S = e\mathbf{E} \cdot \mathbf{s} \times \mathbf{p}/2m^2c^2$.

The number of the diagrams in third-order and higher order is very large. That makes a complete calculation very difficult. In fact it is hardly feasible to go beyond

third-order in this way. In order to investigate the effect of a certain type of interaction in higher-order without handling huge number of diagrams a *coupled-cluster* approach (see e.g. Lindgren and Morrison (1982)) has been developed. Basically this approach is to target a certain type of interaction, say the *pair correlation* (effective two-body interaction), and only to discuss such types albeit to a high order (even to all orders). The Coulomb two-body interaction and so pair correlation is of vital importance in determining the details and even the gross features of the energy level structure. It will also be important in considering intensities of optical transitions, especially under certain circumstances. One-body interactions such as spin-orbit coupling and (for intensities) the matter-radiation interactions are easier to include. Since core electrons are much harder than valence electrons to excite, we can make an approximation: all core excitation diagrams are ignored. This approximation can greatly reduces the number of diagrams without losing the essential of the description of the problem in hand.

Under the approximation of ignoring the core-excitation this diagrammatic method is easier to use for analysing the transition processes, especially for the purpose of investigating the electron-correlation effect, i.e. the role of the Coulomb interaction. In the case of lanthanide intra-configurational transitions, nine Goldstone diagrams up to third-order of perturbation are obtained and they can be used for one-photon, two-photon absorption, and Raman and Rayleigh scattering. The new spin-dependent E1 matter-field operator H'_S can be easily introduced into these diagrams to give a new spin-dependent transition mechanism. Likewise, other new matter-radiation interaction operators obtained from relativistic corrections (see chapter 6) can also be introduced into these diagrams to give still more new mechanisms. The relationship between the Goldstone diagram and its Jucys-type many-electron angular momentum diagram is analysed. A practical example is given for the Goldstone diagram suitable for Judd-Ofelt theory, and I use the angular momentum coupling diagram (the SO_3 group) method to re-derive the Judd-Ofelt result. A simplified approach to derive the angular part of any Goldstone diagram in terms of the effective tensor operators is also discussed.

Along with the Goldstone diagrammatic analysis, a controversy regarding a disconnected effective Hamiltonian diagram obtained by Judd and Pooler (1982) and Downer *et al.* (1988) has been discussed. Being an *unlinked diagram* such a diagram should be cancelled out according to full linked diagram theorem. At this stage

this controversy remains unsettled. The full linkage between time-independent and time-dependent perturbation theory and the related (in different forms) *linked cluster theorems* and the relationship with Abrikosov projection is still not very clear. A deeper investigation is needed.

The special properties of half-filled shells and the ground state splitting of the rhenium atom in krypton matrix are investigated quantitatively. This is a rather complex matter. To induce the reported ground state splitting the higher order (higher than second-order) perturbation which involves many states, even with other configurations, must be considered. Not only the cubic crystal field but also the (non-cubic) axial term should also be included.

The formal connections between quasi-spin, charge conjugation and time reversal have been discussed by Stedman (1987). After our development of the time reversal selection rules obtained in the higher group levels, the possible implication for quasi-spin and charge conjugation is still unclear.

The extension of time reversal selection rules and the corresponding applications of group theoretic method from a fermion system to a boson system, such as nuclear IBM bosons, and/or superconductor is another distant but attractive field to be investigated.

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